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## PROCEEDINGS.

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X. *On the Diffusion of Solutions. By* T. H. LITTLEWOOD,, *M.A., B.Sc., Hon. Research Fellow of University College, Reading.*

ABSTRACT.

An *optical method* is described for finding the *concentration* at various depths in a diffusing solution. The solution is contained in a closed vessel, the top and one side of which are of glass. On the glass side is a vertical scale. This vessel is immersed in another filled with water, which contains a mirror which can be rotated, and the position of which is read on a graduated scale. On a horizontal sliding stand is a telescope, which carries a horizontal wire illuminated by sodium light. The mirror is adjusted so that the image of the wire, after twice passing through the liquid, is seen on the cross wires of the telescope. The corresponding division of the vertical scale is also observed, which can be done to 0·02 mm. These measures enable the concentration to be determined at different depths, with an *accuracy* of about 0·05 gr. per litre.

The second part of the Paper details the *method of calculating the coefficient of diffusion* from a series of measures at different times. It is possible to obtain sufficient data for this in less than a day.

The *results* so far obtained are in good agreement with those obtained by other methods.

SEVERAL years ago the author described to the Physical Society a method of obtaining the concentration at various points in a solution of varying strength at different depths, without disturbing it in any way. (Proc. Phys. Soc., Feb., 1894.)

After a prolonged trial the method proved to be insufficiently sensitive to determine the coefficient of diffusion. Later on a modification of the method was devised which greatly increases the sensitivity, and preliminary results have been obtained with it, which show that it is capable of giving consistent results in good agreement with those obtained by other methods, but in a considerably shorter time.

A method is also described by which the coefficient of diffusion can be calculated from the observations, without making any assumptions as to the previous history of the solution, or as to the nature of the law connecting the observations.

(1) The principle of the method used is as follows. (*See* Fig. 1.) If a solution of a substance is diffusing into water or another solvent, the solution will vary in density at different depths, and we may assume that it consists of a series of horizontal layers, each of the same density at the same depth. Suppose $Aa$ is a narrow pencil of parallel rays of light, incident at $a$ on the upper surface of such a liquid, which is contained in a glass vessel. The face $BC$ of the vessel is approximately vertical. Owing to the total reflection the light will not usually be able to emerge, but on surrounding the vessel by a larger one containing pure water the light will pass through the face. In the larger vessel is a mirror, which can be rotated about a horizontal axis $O$. The mirror is adjusted until the pencil is reflected back along its previous path. The path will in general be a curved line $Aabcdeh$. Suppose now the pencil is moved parallel to itself into the position $A'a'$. Let the new path be $A'a'b'c'd'e'f'h'$. Then the mirror will have to be turned through an angle $hOh'$, in order to reflect the pencil back on its path again. Theory and experiment show that this angle is a function of the difference between the indices of refraction at $e$ and $f$, and to a considerable degree of accuracy, *the angle $hOh'$ is proportional to the difference of the concentrations at $e$ and $f$.*

This may be proved theoretically as follows :—

Calling the angles of incidence and refraction at the upper surfaces of the layers $i_a, r_a$; $i_b, r_b$, &c. ; calling the indices of refraction of the layers $n_a, n_b$, &c., that of air $n$, and that of water $n_0$, and the angle of incidence on the upper surface $i$, we get the equations

$$n \sin i = n^a \sin r_a = n_a \sin i_b = n_b \sin r_b = \&c. = n_x \sin r_x \quad . \quad . \quad . \quad . \quad (1)$$

This shows that the angle of refraction for the layer $x$ is exactly the same as if all the intermediate layers up to the $x$th were eliminated, and the ray passed directly from air into that layer. If $x$ is the layer at which the pencil strikes the side of the vessel it will be refracted out into the surrounding water.

If $R_x$ is the angle of emergence, $n_x \cos r_x = n_w \sin R_x$ , . . . (2)

From (1) and (2) we obtain $n_x^2 = n^2 \sin^2 i + n_w^2 \sin^2 R_x$.
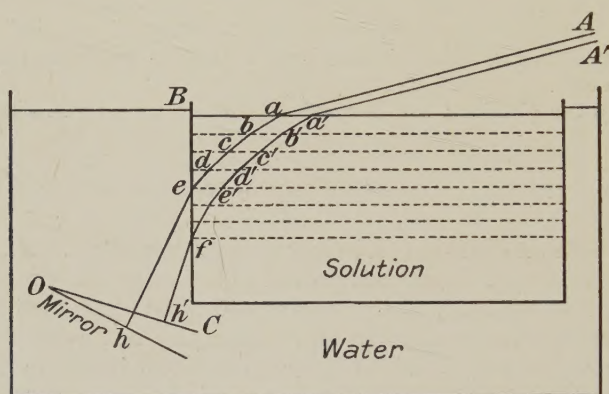


FIG. 1.

If $y$ is the point of exit in another position of the pencil,

$$n_y^2 = n^2 \sin^2 i + n_w^2 \sin^2 R_y.$$

∴ $$n_y - n_x = n \sin i \left\{ \sqrt{1 + \frac{n^2}{n^2} \cdot \frac{\sin^2 R_y}{\sin^2 i}} - \sqrt{1 + \frac{n_w^2}{n^2} \cdot \frac{\sin^2 R_x}{\sin^2 i}} \right\}$$

which is equivalent to our first statement.

Since $n_x$ and $n_y$ only differ slightly, $R_x$ and $R_y$ are also nearly equal. Hence, denoting by $\delta n$ the change in $n_x$, we get

$$\delta n = \tfrac{1}{2}(n^2 \sin^2 i + n_w^2 \sin^2 R_x)^{-\frac{1}{2}} \times 2n_w^2 \sin R_x \cos R_x \, \delta R_x,$$

where $\delta R_x$ is the angle through which the mirror is turned.

Experiment shows that the change in the refractive index is very nearly proportional to the change in concentration. Hence the change in concentration is nearly proportional to the angle through which the mirror is turned.

To get the best effect the incident ray should be at a small angle to the surface.

Experimentally it was found that the proportional law could be assumed for considerable differences in concentration, with very fair accuracy.

From the foregoing discussion it is clear that for any particular concentration there is a corresponding position of the mirror. These positions can be determined for several known concentrations, and other points can be calculated by the proportional law.

If we also know the exact points at which the pencil of light passes through the side of the vessel for each position of the mirror, we are able to trace the state of the liquid through the whole extent.

(2) To carry out the principle experimentally, the pencil of light is obtained by illuminating with sodium light a fine wire, which is placed horizontally close to the object glass of a telescope. In an alternative method, the wire may be at the focus of an auto-collimating telescope. The telescope can be moved parallel to itself along an accurately worked slide. A pair of cross wires is placed exactly



Vertical Longitudinal
Section of Tank.

Vertical Transverse
Section of Tank.
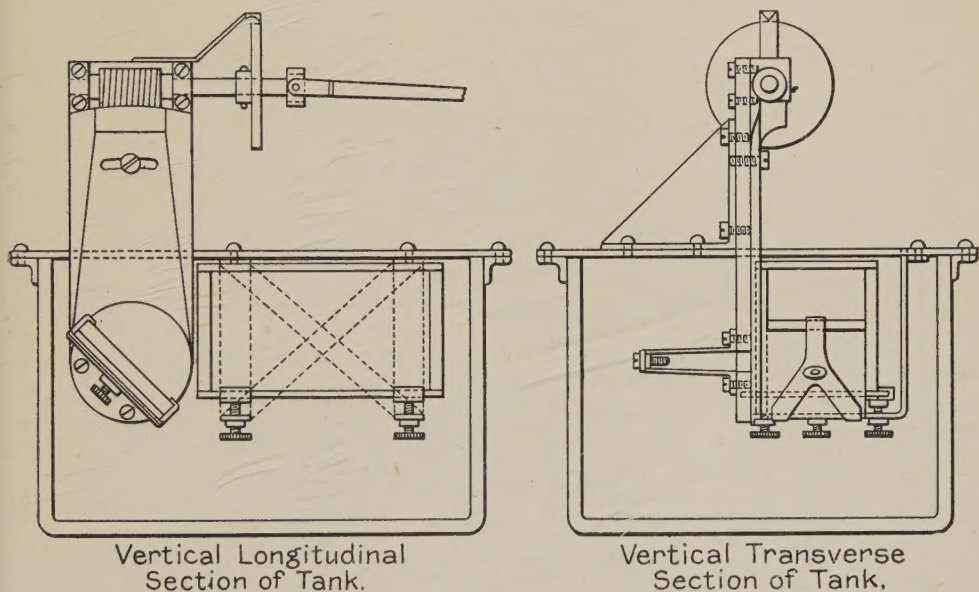
Fig. 2.

in the optical axis of the telescope, and the mirror is turned until the image of the wire falls on the cross wires. On the inner face of the front side of the diffusion vessel a scale of millimetres is engraved. By altering the focus of the telescope, it can be focussed on this scale. The telescope can thus be placed so that the central line of the pencil passes through any desired point on the scale, and the corresponding position of the mirror can be determined for this point.

In the apparatus used (Figs. 2 and 3), the mirror was turned by a worm wheel, the screw head of which was divided into 100 parts. Consecutive readings could be obtained which did not differ by more than one or two tenths of a division, corresponding to an angle of a few seconds. The change in position of the mirror from pure water to a solution of potassium chloride, containing 100 gr. per litre, was about 220 div., so that a change in concentration of 0·05 gr. per litre was measurable. In one hour the change in angle at a fixed depth due to diffusion of such a solution

was about 1½ divisions. The scale displacement of the telescope could be read by a vernier to 1/50 mm., the corresponding vertical change in the depth of the point of exit of the pencil being about as much.

The glass diffusion vessel was $10 \times 5 \times 5$ cm. internal dimensions.

Owing to the curvature of the upper surface, it was necessary to cover it by a plate of glass, in one corner of which was a hole 1 cm. in diameter. The positions of the mirror were first determined for several solutions of known strength. By means of suitably placed stops the vessel could be always replaced exactly in the same position after removal. After calibration the vessel was half-filled with pure water ; the solution in use was then poured in through a long funnel with a fine capillary jet, reaching to the bottom of the tank. When full the hole was closed by a rubber stopper to prevent evaporation. After standing about 24 hours sufficient diffusion had as a rule taken place, to detect the change in concentration in the upper part of the vessel.



Plan of Illuminator.

Sliding Stand, End Elevation.
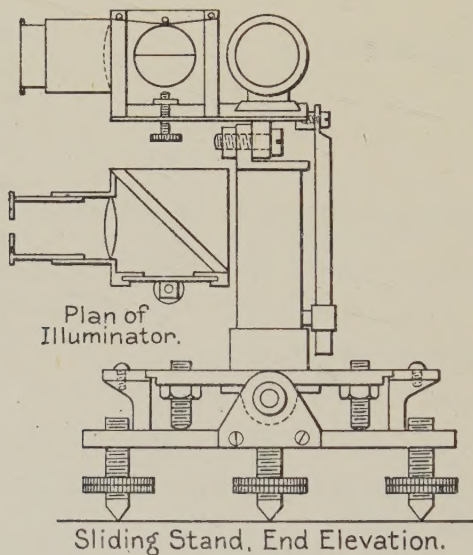
FIG. 3.

The chief cause of inaccuracy in the results obtained was probably the variation of temperature to which the apparatus was subjected. No constant temperature room was available, and the changes of temperature in the course of a few hours destroy the advantages of the sensitivity.

In one day sufficient data can be obtained to enable the coefficient of diffusion of a solution of KCl to be determined. Also measurements can be made simultaneously over the whole range from pure water to a strong solution.

(3) Having obtained the concentration at various depths, the next step is to deduce from its alteration with time the corresponding coefficient of diffusion.

All we shall assume is that it takes place according to the ordinary Fick's law. Then the concentration at a given point at a depth $x$ being $u$, the change in concentration in the time $\delta t$ will be $k \cdot d^2u/dx^2 \cdot \delta t$, where $k$ is the required coefficient.

Suppose that we have measured the values of $u$ at a series of equidistant depths, then by the method of Finite Differences we can calculate the most probable values of $d^2u/dx^2$ at these points. For convenience we shall take 5 points, $a$, $b$, $c$, $d$, $e$, at distances $y$ apart. Then, if $u_a$, $u_b$, &c., are the observed concentrations, it is easy to show that (denoting double differentiation by $''$)

$$u_b'' = \{u_a - 5u_b/3 + u_c/2 + u_d/3 - (u_a + u_e)/12\}/y^2$$
$$u_c'' = \{4u_b/3 - 5u_c/2 + 4u_d/3 - (u_a + u_e)/12\}/y^2$$
$$u_d'' = \{u_e + u_b/3 + u_c/2 - 5u_d/3 - (u_a + u_e)/12\}/y^2$$
$$u_b'' + u_c'' + u_d'' = \{3(u_a + u_e)/4 - 3u_c/2\}/y^2.$$

Hence the total change in the time $t$ at the three given depths will be

$$\frac{3k}{4y^2} \int_0^t (u_a + u_e - 2u_c)dt = \frac{3k}{4y^2} \int_0^t U dt,$$

when $U$ is the value of $(u_n + u_e - 2u_c)$ at any instant.

In a similar manner it can be shown that if we have five observed values of $U$ at equal intervals of time $z$, viz., $U_1$, $U_2$, $U_3$, $U_4$, $U_5$, then

$$\int_0^t U dt = z \{14(U_1 + U_5) + 64(U_2 + U_4) + 24U_3\}/45.$$

But obviously the sum of the changes in concentration at the three depths is also equal (denoting times by numerical suffixes) to

$$u_{b \cdot 5} - u_{b \cdot 1} + u_{c \cdot 5} - u_{c \cdot 1} + u_{d \cdot 5} - u_{d \cdot 1}.$$

Hence, by dividing this result by $\dfrac{3}{4y^2} \int_0^t U dt$, we obtain $k$.

This method assumes nothing as to the real nature of the distribution in the liquid, but only that it has the actual observed values. As for the small range of values which alone are considered in an actual experiment, the proportional law will hold, $u_a - u_c$, &c., will be equal to change of angle $\times$ a constant. In the final division this constant will appear in both numerator and denominator, and therefore will divide out. It follows that we need do no more than use in the calculation the angular positions of the mirror, expressed in any units we like. These considerations considerably simplify the numerical work.

(4) As in the preliminary experiments no thermostatic room was available, the results so far obtained are not very valuable. The following set of observations will illustrate the method.

*Sol. of KCl.* 100 grs. *per litre diffusing into pure water. Temp.* 16°—17·8°. *Readings of mirror scale (prop. to conc.).*

| Depths in cm. | At start. | After 2 hours. | 4 hours. | 6 hours. | 8 hours. |
|---|---|---|---|---|---|
| 0·7 | 3·2 | 7·2 | 10·1 | 13·3 | 16·5 |
| 1·0 | 9·7 | 13·5 | 16·4 | 19·9 | 23·0 |
| 1·3 | 19·0 | 22·5 | 25·6 | 28·0 | 31·5 |
| 1·6 | 30·5 | 33·7 | 36·4 | 39·3 | 42·6 |
| 1·9 | 45·0 | 48·1 | 50·0 | 52·6 | 54·5 |
| $U=$ | 10·2 | 10·3 | 8·9 | 9·9 | 9·0 |

$$y = 0 \cdot 3 \text{ cm.} \qquad z = 2 \times 3600 \text{ secs.}$$

Sum of changes of ordinates$=13\cdot3+12\cdot5+12\cdot1=37\cdot9$ cm.

$$\int_0^t U dt = 2\cdot84 \times 10^5$$

$$K = \frac{37\cdot9 \ \times 4 \times 0\cdot09}{2\cdot84 \times 3 \times 10^5} = 1\cdot601 \times 10^{-5} \text{ at average temperature } 16\cdot9°.$$

A similar solution at $19\cdot5°$ gave $k = 1\cdot625 \times 10^{-5}$.

These results do not differ widely from those obtained by other methods.

### DISCUSSION.

Mr. B. W. CLACK expressed his satisfaction at meeting for the first time another worker in the subject which had engaged his own attention for a number of years. Other experimenters have attempted to measure the angle $R^x$, but the author goes further and measures the rate of change of this quantity with time. This is only of the order of $1'$ per hour, and strikes one as a difficult matter to determine with certainty. The change $\delta R$ is taken to be proportional to the change $\delta n$. Is this assumption justifiable? It would appear to lead to the conclusion that $dn/du$ is also constant, whereas in the speaker's experience variations of 20 per cent. might occur. He expressed the view that the method of the author might be improved by adapting it to the case when the steady state has been attained.

Dr. A. GRIFFITHS hoped the author would continue his experiments so as to accumulate a body of consistent results. He would like to suggest the possibility of Fick's hypothesis being inadequate to account for the facts of diffusion.

Mr. T. SMITH considered it very doubtful whether really accurate results were possible with the type of optical method adopted. In a matter of the measurement of seconds of angle very special precautions were required. He thought that an interference method would get over the difficulty. In regard to the theory involved in the calculation it would be an advantage to substitute the method of waves for that of rays, since the latter often leads to wrong conclusions.

Dr. J. S. ANDERSON asked the minimum difference of refractive index measurable by the author, and whether dispersion caused trouble.

The AUTHOR, in reply, said that the conclusion that $\delta R$ was proportional to $\delta n$ was based on the experimental results. He thought that the method of calculation might be modified so that the assumption of the constancy of $k$ would not be necessary. In regard to Mr. Smith's remarks the greatest care was taken to ensure rigidity of the apparatus; the separate portions were bolted down to a thick marble slab, and thus far consistent results had been obtained. In regard to the theory, he had considered that the shortness of optical path justified the use of the ray method. As to sensitiveness, he had not calculated it out in terms of refractive index, but in terms of concentration he was able to detect a change of $0\cdot05$ gr. of salt per litre. No trouble in regard to dispersion was met, using sodium light for the illuminant.

XI. *On a Special Apparatus for the Measurement at Various Temperatures of the Thomson Effect in Wires.* By H. REDMAYNE NETTLETON, *M.Sc.* (*Lond.*), *Lecturer in Physics at Birkbeck College.*

## ABSTRACT.

In 1916 (Proc. Phys. Soc., Vol. XXIX., p. 59) the author outlined a *steady state null method* for measuring the Thomson effect in short lengths of wire. The present Paper describes a convenient form of apparatus for carrying out measurements with rapidity and under good theoretical conditions. The short wire under test (S.W.G. 18) passes through *electrical heaters* which may quickly be brought to and maintained at steady temperatures differing by some 50°C. over the *range* 20°C. *to* 250°C. A short coil of the finest double silk-covered copper wire (S.W.G. 44) acts as the Thomson-Joule heat detector. Test experiments were performed with *iron* and *constantan* wires, yielding values of the Thomson effect at various temperatures over the range indicated. Many improvements in the method are described, chief among which is a greatly improved sensibility.

## I.—*Introduction.*

IN 1916 the author described (Proc. Phys. Soc., Vol. XXIX., p. 59, 1916) a method of measuring the Thomson effect in wires based upon a steady state form of application of the Le Roux-Haga principle. Owing to war conditions and the time given to theoretical study and to the finding of the best conditions of working, progress has until recently been slow ; but the writer is now able to describe fully a special apparatus on the development of which he has been occupied during the last three years, and which rapidly and with close conformity to good theoretical conditions enables the Thomson effect to be measured in wires. The use of the apparatus is illustrated by experiments on specimens of constantan and iron wires over the range 50°C.-200°C. Other important improvements in the method, chief among which is a greatly increased sensibility, are also described here.

## II.—*Theory of the Method.*

The essential theory of the method is given in the author's previous Paper (*loc. cit.*). A further and more detailed study of the limitations of the Le Roux-Haga principle in general has convinced the writer of the many advantages of still adhering to a rapid but, none the less, steady state form of application of this principle and, more particularly, of always maintaining the thermometric detector with its centre of symmetry in the middle of the portion under gradient of the conductor to be tested. Under such conditions the usual Joulean alternations and the Thomson reversals become merged into one operation ; the sensibility is always a maximum ; the size of the bolometer coil is no disadvantage ; the secondary effects of Joulean heating are of minimum trouble, and, what is most important, the temperature coefficients of resistance and of the Thomson coefficient admit of the most simple interpretation in the formula of the method, given in section 4 below, which may be applied with a higher accuracy than more complex formulæ under other conditions. In particular, the determination of the ratio $R/U$ (of resistance of wire to temperature difference between its ends) is not only practically more simple but theoretically better than that of measuring the usual ratio $w/\dfrac{d\theta}{dx}$, where $w$

is the resistance per unit length of the conductor in the neighbourhood of the detector and $d\theta/dx$ the corresponding local temperature gradient.

Accordingly, the apparatus described below is so constructed that both constant temperature sources (and not one only) may be raised in temperature until they differ by some 50°C., and the Thomson coefficient measured is always that corresponding to the mean temperature of the disc-ends of the wire.   Since either heater may be made the hotter, the Le Roux longitudinal interchange of the ends of the conductor for the detection and elimination of heterogenity may easily be effected without disturbing the wire and its surroundings.
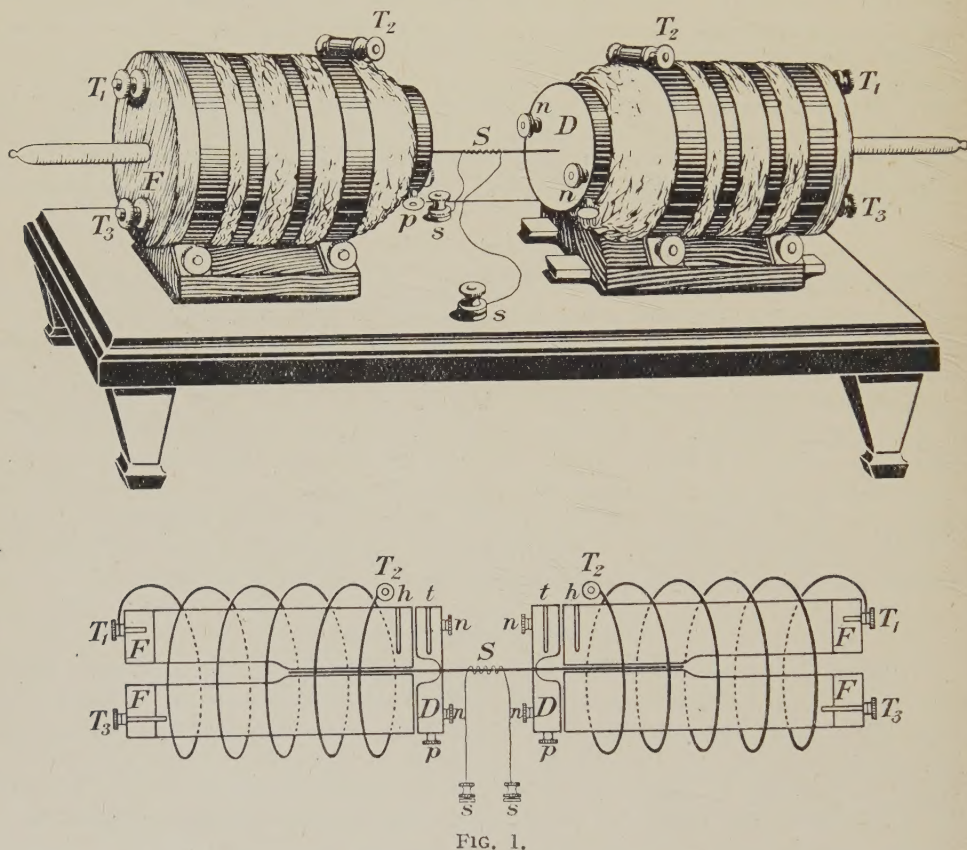


FIG. 1.

III.—*Description of the Apparatus and of the Mounting of the Experimental Wire.*

The general appearance and the essential features of the apparatus will be understood from Fig. 6.   Solid copper cylinders of length 7·5 cms. are turned down to a diameter of 4·8 cm. and constitute the electrical heaters when wound with several turns of nichrome wire, s.w.g. 24, separated from them by thin mica. These heating coils are brought on the one hand to the terminals $T_1$ which are let in to the fibre casings $F$, and on the other hand to the terminals $T_2$ mounted on fibre rods which are themselves let in to the copper cylinders.   Each copper cylinder is drilled centrally for half its length with a hole of just sufficient diameter to receive

a thermometer, 0°C.-360°C., with which to ascertain its approximate temperature ; for the other half it is drilled with a fine hole just sufficient to permit the entry of the experimental wire of s.w.g. 18. The cylinders, after winding are covered with asbestos strapped on as shown in the figure and are suitably mounted on a base board ; the distance between them may be varied at will as the right-hand cylinder may be clamped in any position along its sliding rails. The terminals $T_3$ pass right through the fibre casing and are thus in conducting communication with the copper. The fine holes at $h$ permit the insertion of thermo-junctions.

The copper discs $D$ into which the experimental wire is soldered are of thickness 5 mm. and of diameter identical with that of the heaters : they resemble in appearance the ends of the preliminary apparatus (shown in Fig. 3 of the author's earlier Paper) and the cavities leading to the central holes—which just permit the passage of the wire—are carried as deep as possible. Each disc is drilled at $t$ with a
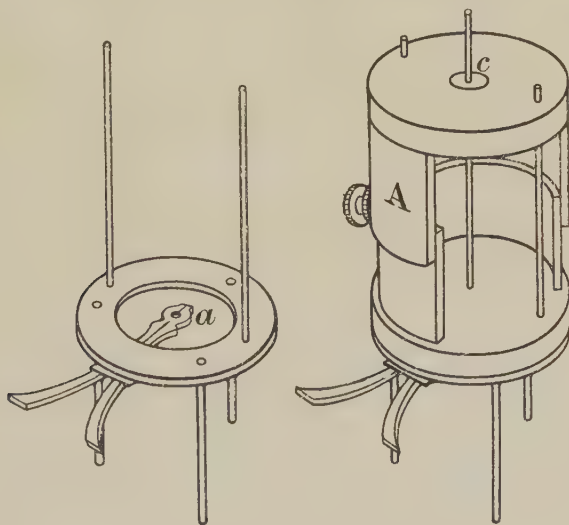


FIG. 2.

fine deep vertical hole of diameter 2 mm. to permit the insertion of a thermo-junction, while transverse holes allow the disc to be brought into good surface contact with the corresponding copper heater by slipping the former over screws let into and projecting from the latter and then tightening up with nuts $n$, $n$. Terminals at $p$, $p$ serve for potential leads wherewith to measure *in situ* the resistance of the operative part of the wire.

The soldering of the experimental wire into its isothermal and equipotential " disc-ends " is greatly facilitated by use of the special soldering stand seen in Fig. 7. For the discs being placed upon it in position and separated to the desired extent by means of the adjustable separator $A$, and the wire being passed through the discs and clamped at $a$ when suitably situated, solder is applied at the cavity $c$ which is easily accessible to the blowpipe. The discs, wire and separator are then slipped off the soldering stand, inverted as a whole and replaced (the clamp $a$ being now pushed to one side) and the soldering of the wire into the other disc is then effected. As the melting point of the solder sets a limit to the temperature of the investigation,

solders other than those containing only lead and tin have been experimented with. Aluminium solder (altior brand) when used with a zinc flux has proved very satisfactory for fixing the iron and constantan wires used in this investigation. Since the detecting coil is now wound on the wire after fixing it to the copper discs, it should be possible, if desired, to use a silver solder.

The detecting coil $S$, Fig. 6, is of silk-covered copper wire, s.w.g. 44, the diameters of the bare and covered wire being only 0·07 mm. and 0·14 mm. respectively ; it is wound symmetrically as a thread-like covering around the middle of the operative part of the experimental wire and over about one-third of its length. To effect this use is made of the lathe, the one disc being clamped in the main revolving chuck and the inoperative part of the wire protruding some 4 cm. from the back of the other disc resting loosely in a tube held by the small fixed chuck. Lengths of detecting coil wire are left protruding to effect connection with the insulated double terminals $s, s$, while the coil itself is lightly varnished to prevent displacement or uncoiling.

The operative part of the experimental wire is now wound with two or three layers of silk yarn (unless temperatures above 250°C. are aimed at, when asbestos thread should be substituted) and then further protected with wool. The wire and discs are now ready for mounting on to the main apparatus, in effecting which the protruding and inoperative portions of the wire are slipped through the narrow central holes in the copper heaters against which the discs are now brought into good surface contact. After screwing up tightly the nuts $n, n$, the heaters are pulled and clamped as far apart as possible in order to keep the wire straight. Cotton wool or asbestos wool is now freely supplied to any exposed parts of the discs and heaters in order to adequately allay convection currents.

### IV.—*Outline of Experimental Order.*

To perform an experiment the electrical heaters are first raised to the desired approximately constant temperatures which may differ from one another by from 20° C. to 80° C., according to the sensibility of the specimen under investigation. A constant electric current $C_1$ of some two amperes derived from accumulators is then passed through the experimental wire from hot to cold, being admitted and leaving by the terminals $T_3$ (Fig. 6). When the steady state is attained this current is reversed and at the same time slightly raised in magnitude (assuming $\sigma$ is positive) to such a value $C_2$ found by trial that causes, when in a minute or two the new steady state is attained, no change in the thermometric effect on the resistance of the detecting coil $S$. The small current difference $C_2-C_1$, referred to hereafter as the balancing current, is measured directly in a shunt circuit on a Cambridge thermo-electric potentiometer, which serves also a moment afterwards to measure the temperatures as recorded by insulated thermo-junctions in the disc holes $t, t$ and so the difference of temperature $U$ between the disc ends of the wire. Lastly, with the electrical heaters still maintained at their respective " hot " and " cold " temperatures the resistance $R$ of the wire under gradient is measured *in situ*—again on the same potentiometer now in communication with the disc terminals $p, p$. The length of wire having been shown in the previous Paper to be sufficiently short to neglect the effect of emissivity, the Thomson effect $\sigma$ at the mean temperature of the disc ends is given by

$$\sigma = R/JU \ . \ (C_2-C_1),$$

where $J$ is the number of joules equivalent to one calorie.

V.—*The Essential Connections, Operations and Measurements.*

(*a*). The electrical heating.

Both electrical heaters of about 5 ohms resistance are provided with shunts consisting of sliding rheostats of range 0-100 ohms. They may thus be put together in series with appropriate resistances permitting a current of from 0-4 amperes when
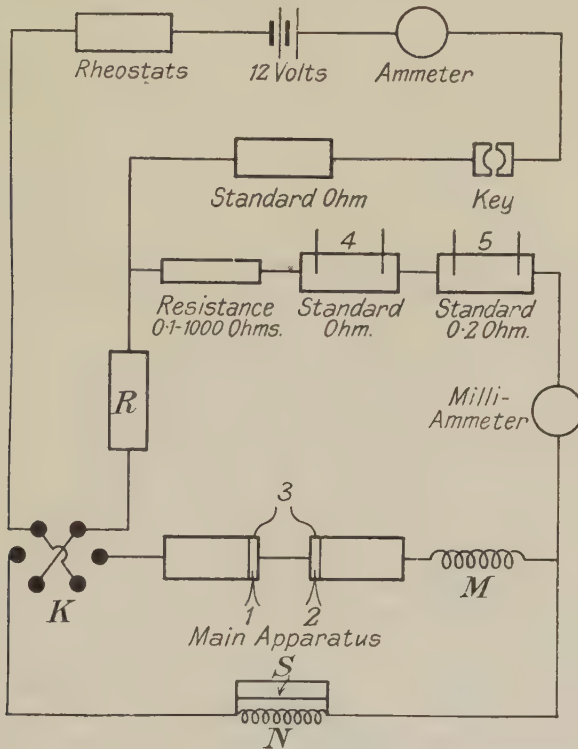


FIG. 3.

joined to the 100-volt mains. Usually the current so derived is sufficiently constant during the time of proving a final balance to yield a sensibly steady state as recorded by the detecting coil, though secular changes are, of course, neutralised as far as possible at appropriate moments with the aid of the fine adjustment main rheostat or with the heating coil shunts. Though only giving the approximate temperatures the thermometers in the copper heaters are very useful. The electrical heating on the whole is very satisfactory and it is easy with practice rapidly to reproduce in a heater any desired temperature and to then adjust the current to maintain this temperature constant.

(*b*). The main electrical connections.

The electrical connections shown in Fig. 8 are somewhat more convenient than those of the earlier arrangement, for a single key *K* not only effects the commutation of the current, but at the same time produces the necessary change in its magnitude.

The main circuit consists of accumulators (12 volts), an ammeter, rheostats, a standard ohm, the specially designed low-resistance commutator $K$, the main apparatus and the approximate ohm $M$ and the dummy apparatus, viz., the ohm $N$ shunted by the rheostat $S$. The shunt circuit includes a milli-ammeter, a resistance box 0·1 to 1,000 ohms, a standard ohm and a standard 0·2 ohm. As the standard ohm is only required in the main circuit during a resistance measurement—in which case the shunt circuit is not used—it is arranged that it may be completely switched over from the one circuit to the other.

By means of the rheostat $S$ it is easy to secure accurate equality of resistance between on the one hand the main apparatus, the ohm $M$, the operative part of $K$ and the rheostat $R$ and on the other hand the shunted ohm $N$, the now operative part of $K$ on switching over and again the common rheostat $R$, so that no matter which of these portions is shunted by the branch circuit the latter is traversed by one and the same current as tested by the equality of potential differences across the standard 0·2 ohm. Under such circumstances, moreover, it is clear that the magnitude of this shunt current is necessarily equal to the difference in magnitude between the larger currents traversing the main apparatus before and after rocking over the commutator $K$. When now by adjusting the resistance of the shunt circuit a branch current $C_2 - C_1$ has been obtained, which is such as to maintain thermal equilibrium in the detecting coil on operating the commutator $K$, its magnitude is measured by finding on the potentiometer the milli-volts across the standard ohm or more usually across its known sub-multiple, the standard 0·2 ohm.

Special five-way copper plug keys connected to the Cambridge thermo-electric potentiometer enable the various potential differences which have to be measured during an experiment to be switched quickly on to this instrument.

(c). The calibration of the thermo-junctions and the measurement of $U$, the difference of temperature between the wire disc-ends.

The thermo-junctions, which we may call $A$ and $B$, are of iron and constantan and are insulated with ohmaline varnish. They dip deep into the disc holes $t$, $t$ (Fig. 6) containing mercury and are so paired against a similar cold junction $C$ that either of the couples $A-C$ or $B-C$ may at any moment be switched on to the thermo-electric potentiometer. From the millivolts recorded and from the temperature of $C$ together with the data derived from previous calibration, the actual disc-end temperatures are readily ascertained. The junctions of the iron with the copper connecting leads are side by side in glass tubes under water.

The thermo-couples $A-C$ and $B-C$ were most carefully calibrated against a platinum thermometer by immersing $C$ in melting ice and bringing $A$ and $B$ (placed alongside the platinum bulb) to numerous steady temperatures up to 270° C. in a large electrically-heated and mechanically-stirred tank containing oil of high flash point. The maximum difference in the readings for the two thermocouples for the same temperature interval very rarely exceeded 1 part in 2000, and the electro-motive force in microvolts for either couple for the interval 0°C. — T°C. was expressed as a result of the calibration by the empirical relation :—$E/T = 51·85 + 0·0331T - 0·00007T^2 + 0·000,000,044T^3$.

(d). The measurement of the resistance of the wire.

This is carried out as in the previous Paper with the aid of a constant current of 1·018 amperes save that the wire is maintained under its temperature gradient. Though the millivolts across the terminals $p$, $p$ now differ considerably with the

direction of the standard current, the mean value is independent of the electromotive force of the thermo-couple formed by the wire and the copper potential leads. Between the terminals $p, p$ and the potentiometer is a plug commutator which must be switched over when the standard current is reversed.

(e). The detecting coil connections and the marked improvement in the sensibility.

In a Paper on " Electrical recording thermometers for clinical work " Callendar (Proc. Phys. Soc., Vol. XXII., p. 220, 1910) has investigated the conditions of sensibility in measuring a resistance by the Wheatstone bridge method where, as in the case of electrical thermometry, the limiting condition is imposed by the heating effect of the current on the resistance to be measured. In the light of this investigation a vast improvement in sensibility is attained by interchanging the galvanometer and battery in the Maxwell arrangement shown in Fig. 5 of Part IV., p. 25. For taking these $G=10$ ohms and $S=5$ ohms, so that $X=500$ ohms, we may show that the current $c$ through the galvanometer when the balanced detecting coil, traversed by a heating current $C$, alters in resistance by an amount $dS$ is given by $c=C.dS/520$, which expresses the Maxwell sensibility. On interchanging galvanometer and battery, however, and raising the voltage so as to secure the same limiting heating current $C$, we have for the new arrangement a sensibility given by $c=C.dS/25$ which is over 20 times better. Alternatively if we connect the detecting coil to a pyrometer bridge with equal ten-ohm ratio arms we find $c=C.dS/35$, which is nearly 15 times superior to the Maxwell arrangement.

Considerations such as these have led the writer to abandon the early arrangement, and the detecting coil $S$ is now connected directly to a pyrometer bridge with 10-ohm ratio arms which, though not yielding the maximum sensibility attainable, marks the immense improvement already stated, requires no increase of voltage, is convenient and is seen to good advantage as the detecting coil resistance becomes greater at higher temperatures. The source of E.M.F. in the pyrometer bridge is a 2-volt accumulator, and the battery circuit is closed throughout an experiment to maintain constant the Joulean heating effect in the thermometric detecting coil; when $S$ is small, 2 or 3 ohms are put in series with the accumulator. The galvanometer is the low resistance Broca instrument used in the previous research, and similar precautions to those already described are taken when finding and confirming the value of the balancing current.

As a concrete example of the sensibility a full scale deflection of 50 cm. was obtained in 30 seconds on reversing (but not altering in magnitude) a current of 2 amperes in constantan wire with its extremities differing in temperature by 60°C.

### VI.—*Illustration of the Method by a Typical Experiment.*

All experiments were performed in a manner similar to that shown for the typical experiment below, for which all essential data are given. The readings on the thermo-electric potentiometer (T.E.P.) are in millivolts :—

### AUGUST 8, 1921. IRON WIRE.

5.30 A.M.—Electrical heating commenced.

6.0 A.M.—Heaters reached 84°C. and 134°C. respectively.

6.30 A.M.—Heaters steady at about 84°C. and 134°C. Steady current of about 2 amperes commenced in wire.

7.0  A.M.—Detecting coil resistance stationary at about 9·6 ohms under steady state. Search for balancing current commenced.

7.45 A.M.—Balance confirmed after repeated tests. Balancing current as shown by milliammeter 0·110 amperes. Readings on T.E.P. across 0·197 ohm : $\begin{array}{l}\rightarrow 21\cdot610 \\ \leftarrow 21\cdot590\end{array}$

7.47 A.M.—Thermometric observations :—

|  | T.E.P. reading for thermo-couples. | Thermometer reading. |
|---|---|---|
| Hot end   ...   ...   ...   ... | 6·440 | ... 133·8°C. |
| Cold end  ...   ...   ...   ... | 3·610 | ... 84·4°C. |
| Cold Junction   ...   ...   ... | — | ... 19·2°C. |

7.50 A.M.—Current through wire altered to 1·0183 amperes.

8.5  A.M.—Potential differences across disc-ends of wire on T.E.P. $\begin{array}{l}\rightarrow 7\cdot290 \\ \leftarrow 8\cdot062\end{array}$

### Conclusion of Experiment.

This experiment yields for the balancing current a value $C_2-C_1=0\cdot02160/0\cdot197 =0\cdot109_6$ ampere, and for the resistance of the wire under gradient a value $R=\frac{1}{2}(0\cdot007290+0\cdot008062)/1\cdot0183=0\cdot00753_8$ ohm. In order to evaluate the temperatures, 1·007 millivolts—the E.M.F. between 0°C. and 19·2°C. as found from the calibration curve—must be added to the readings 6·440 and 3·610 respectively. From the aggregates and the calibration data we easily obtain the corresponding temperatures, viz. : 135·02°C., and 85·20°C., giving the temperature difference $U=49\cdot8_2$°C. Whence taking $J_{20}=4\cdot18$ joules per calorie we have :—

$$\sigma_{110}=(0\cdot00753_8\times0\cdot109_6)/(4\cdot18\times49\cdot8_2)$$

$$=3\cdot97\times10^{-6}\text{ calories per coulomb per 1°C.}$$

The same standard ohm is used essentially in the measurement of $C_2-C_1$ as well as in the determination of $R$ ; its absolute value is therefore unimportant.

### VII.—Results of Experiments on Specimens of Constantan and Iron Wire.

TABLE I.—*Results of Experiments on Constantan Wire.*

| Higher temperature. | Lower temperature. | Diff. of temp. $U$. | Balancing current in amps., $C_2-C_1$. | Resistance of wire in ohms, $R$. | Temp. at which $\sigma$ is measured. | $\sigma\times10^6$ in calories per coulomb. |
|---|---|---|---|---|---|---|
| 80·38 | 19·80 | 60·58 | 0·0738 | 0·02015 | 50·1 | 5·87 |
| 80·04 | 20·19 | 59·85 | 0·0728 | 0·02020 | 50·2 | 5·88 |
| 110·63 | 50·07 | 60·56 | 0·0753 | 0·02016 | 80·4 | 6·00 |
| 140·82 | 80·39 | 60·43 | 0·0762 | 0·02016 | 110·6 | 6·08 |
| 171·66 | 111·81 | 59·85 | 0·0760 | 0·02018 | 141·7 | 6·13 |
| 201·60 | 143·44 | 58·16 | 0·0749 | 0·02017 | 172·5 | 6·22 |
| 232·60 | 174·40 | 58·20 | 0·0750 | 0·02020 | 203·5 | 6·23 |

TABLE II.—*Results of Experiments on Iron Wire.*

| Higher tempera-ture. | Lower tempera-ture. | Diff. of temp. $U$. | Balancing current in amps., $C_2-C_1$. | Resistance of wire in ohms. $R$. | Temp. at which $\sigma$ is measured. | $\sigma \times 10^6$ in calories per coulomb. |
|---|---|---|---|---|---|---|
| 73·97 | 22·33 | 51·64 | 0·0915 | 0·006048 | 48·2 | 2·56 |
| 74·93 | 24·94 | 49·99 | 0·0910 | 0·006010 | 49·9 | 2·62 |
| 104·87 | 54·06 | 50·81 | 0·1032 | 0·006786 | 79·5 | 3·30 |
| 135·02 | 85·20 | 49·82 | 0·1096 | 0·007538 | 110·1 | 3·97 |
| 166·17 | 114·75 | 51·42 | 0·1184 | 0·008327 | 140·5 | 4·59 |
| 197·86 | 147·39 | 50·47 | 0·1191 | 0·009172 | 172·6 | 5·18 |
| 230·24 | 179·36 | 50·98 | 0·1200 | 0·010111 | 204·9 | 5·69 |

The results for the constantan over the range of temperature investigated may within the errors of experiment be expressed by the formula :—

$$\sigma_T \times 10^8 = 564 + 107T/200 - 12T^2/10,000$$

The results for iron may likewise be summarised in the form :—

$$\sigma_T \times 10^8 = 138 + 505T/200 - 21T^2/20,000 - 5T^3/10^6$$

## VII.—*Conclusion.*

### DISCUSSION.

Mr. C. R. DARLING congratulated the author on his neat apparatus, and said he looked forward to the accumulation of results which would be of value in settling some of the apparent anom-alies in thermo-electricity. The junction of the two materials considered in the Paper furnished a case in point. It is well known that these yield a very closely linear relation between E.M.F. and temperature-difference, leading, on the usually accepted theory, to the inference that the two Thomson effects cancel, whereas they are found in the present experiments to be different in numerical value. Another example was described in a Paper read by the speaker before this Society a few years ago ; in this case both the Peltier and the Thomson effects were (on the usual theory) to be regarded as zero, whereas the combined thermo-E.M.F. actually observed was 13 millivolts. He hoped that the author's experiments would provide data enabling these matters to be tracked to their true causes.

Mr. F. E. SMITH said it was difficult to understand why the author abstained from the use of the Wheatstone bridge in the determination of his resistance, since this was quite feasible and would undoubtedly lead to greater precision in the determination.

From the AUTHOR (communicated) : In reply to Mr. Darling—the author hopes to measure carefully the Thomson effect in several metals, and to find the thermo-electric power of the same specimens. He has for long been interested in the apparent anomalies mentioned. In nearly all methods of measuring the Thomson effect the error increases with the temperature. The results of the present Paper for the iron and constantan specimens used do not seem seriously out of joint with the electromotive force-temperature curve of the different iron-constantan couples used for the temperature measurements. In reply to Mr. F. E. SMITH—it was very convenient to be able to use, in a limited space and with the apparatus available, the Cambridge thermo-electric potentiometer for the measurements of $R$, $U$ and $C_2-C_1$. Moreover, by its use in the manner described, the value of the standard ohm became unimportant. The resistance of the wire of the order of 1/100 ohm was measured while under temperature gradient, and the accuracy is probably far more than sufficient in view of the limitations imposed by the sensibility in de-termining the balancing current. The author is grateful to Mr. F. E. Smith for his remarks, and will consider the Wheatstone bridge suggestion before making further measurements.

XII. *A Defect in the Sprengel Pump: Its Causes and a Remedy.* By JOHN J. MANLEY, *M.A., Research Fellow, Magdalen College, Oxford.*

## ABSTRACT.

This communication deals with the limitations and irregularities of the Sprengel pump, resulting from the presence of *air skins* upon the interior surfaces. An elaborated form of the pump is described ; also a plan whereby the usual gas skin may be so greatly reduced as to become a negligible quantity. The efficiency of the new pump is markedly superior to that of the older forms, and appears to remain practically constant. Two useful adjuncts to the pump are illustrated and described.

WHEN using a Sprengel pump for producing and maintaining vacua of the order of 0·00004 to 0·00001 mm., I frequently observed that continued pumping caused an increase rather than the expected decrease in pressure. This at first appeared inexplicable, but close observation showed that the growth in the pressure was due to the introduction of air. The pump being in action, minute bubbles of air were seen forming here and there upon the surface of the tube through which the mercury was ascending. Such bubbles originated, or became visible, only at points situated a little below the entrance to the fall-tube ; their number and the rapidity with which they formed were greatly increased by tapping the tube. As the bubbles moved upwards, their rather sudden enlargement suggested that the increase in volume was not wholly due to the diminishing pressure of the mercury column, but that it was to some extent caused by the acquisition of other air from the film upon the tube. It is highly probable that the defects here noted are common to all Sprengel pumps.

In the formation of a film upon glass, the weight of the gas absorbed by the growing film will be dependent upon at least four variables—viz., (1) the variety of the glass and the condition of its surface ; (2) the nature of the gas ; (3) the pressure ; and (4) the temperature. In addition, the weight of the film may be affected by the time allowed for its complete formation. When for a given pressure, &c., an air-film is in a state of equilibrium with respect to the free gas, then on reducing the pressure this equilibrium is destroyed, and the tension of the film left superior to the pressure of the residual gas ; and, as an inevitable result, there follows a continuous decrease in the mass of the film on the one hand, and a corresponding increase in the pressure of the gas on the other. Preliminary experiments have shown that for the restitution of equilibrium between the film and its parent gas a very considerable period is required. This period has not yet been determined ;* but, whatever its duration may be, I find that a marked shortening is effected when the tubes are lightly tapped with a wooden mallet. The beneficial influence of tapping is due to the fact that a vibrating surface throws off catapult-wise some of the film with which it is normally clothed ; but as the vibrations cease the film thus attenuated is rebuilt. The correctness of the several statements just made may be verified with the aid of a sensitive McLeod gauge.

Starting with a chemically clean and empty pump, we may suppose that the internal surfaces possess air-films having approximately maximum values. On the introduction of mercury, the films are to a large extent covered and imprisoned

* The actual measurement of the period is at present receiving attention.

and their subsequent removal or escape is slow and difficult ; more especially is this so when, with the pump in action, the mercury flows but feebly, but with a vigorous flow a marked erosive action is obtained ; consequently, the air-film is speedily worn down to the point at which the erosive power of the mercury is balanced by the attractive force of the glass. If, now, the flow of the mercury is reduced to a normal rate, the efficiency of the pump is found to be high ; ultimately, however, air bubbles re-form at the head of the fall-tube, and the effectiveness of the pump again becomes uncertain. The new bubbles are probably formed by air first eroded and then brought upward from the lower films by the stream of mercury. The defect can, of course, be again temporarily and most quickly remedied by the use of a rapid stream of mercury aided by a simultaneous tapping of the tube. I here omit all remarks as to the probable existence of films upon the mercury, and do not consider the possible adsorption of air by the metal ; these omissions do not materially affect the argument and conclusions. I proceed to show how the difficulty was success-fully met.

First, the new form of the Sprengel pump shown in the figure was designed and built in sections ; these having been chemically cleaned and dried, were subsequently fused together, the completed apparatus conveniently mounted, and the pump was then prepared for action in the following way :—

The tap $t_1$ and the opening $Q_1$ were closed, and pure and dry carbon dioxide passed through the apparatus by way of the tube $A$ ; meanwhile the whole of the glass, with the exception of the cisterns and traps, was strongly and continuously heated. The pump was then allowed to cool whilst the gas was still passing through it. By this plan skins of carbon dioxide were substituted for those of air upon the interior surfaces of the apparatus. The application of a flame to the taps and their immediately adjacent parts being unsafe, the heating of the main body of the pump was somewhat prolonged in order that the air skins within those portions not directly heated might be removed by the stream of hot carbon dioxide. Referring to the diagram above, and knowing that the density of carbon dioxide is decisively superior to that of air, it is at once evident that the major portion of the gas flowing through the chamber $M_1$ escapes through the fall tube, and very little by way of $XO$ and $K$ ; that which passes through the upper limb and into $H$ is wholly insignificant, and may be reduced almost to zero by closing $L$. Hence, during these operations, the solid potash in $H$ is scarcely affected. The carbon dioxide escaping through $Q_2$ is regulated by the taps $t_2$ and $t_3$. When the apparatus was cold, all five exits were temporarily closed, the plug removed from $Q_1$ and the bulb $C$, containing solid potash heated to destroy the air skin within. As soon as the air in $C$ had been removed by carbon dioxide a Geryk pump was attached to $Q_1$ and mercury admitted from the reservoir $R$ into the tube $A$ in quantity sufficient at a later stage nearly, but not quite, to fill the tube $J$. Next, the taps $t_1$, $t_2$ and $t_3$ were closed, and the whole apparatus exhausted as highly as the Geryk pump permitted ; the bulb $C$ was then hermetically sealed by the application of a blowpipe flame directed upon the bend above $Q_1$. During this process all mercury-free tubes were re-heated. At this stage the cistern $E$ was half-filled with mercury by partially opening $t_2$ for a moment ; then $t_2$, having been closed and $t_3$ opened, mercury ascended the tube $Y$, and thus ensured the maintenance of the vacuum in the bulb $B$. Finally, the tubes leading into and out of the cylindrical chamber $D$ were filled with mercury run into them from $R$ ; the pump was then allowed to remain at rest for a few days, after which the tube $L$ was opened and the apparatus to be exhausted fused to it. The potash in the bulb $C$, as well

as that in the drying chamber $H$, was re-fused, allowed to solidify, and then broken up just before being introduced into the containing vessels of the pump. Whilst the pump was resting, the residual carbon dioxide in $D$ and $C$ would be ab-sorbed by the potash in $C$, and the gas pressure reduced to zero, or nearly so. Here it may be remarked that during the removal of the air skins the carbon dioxide
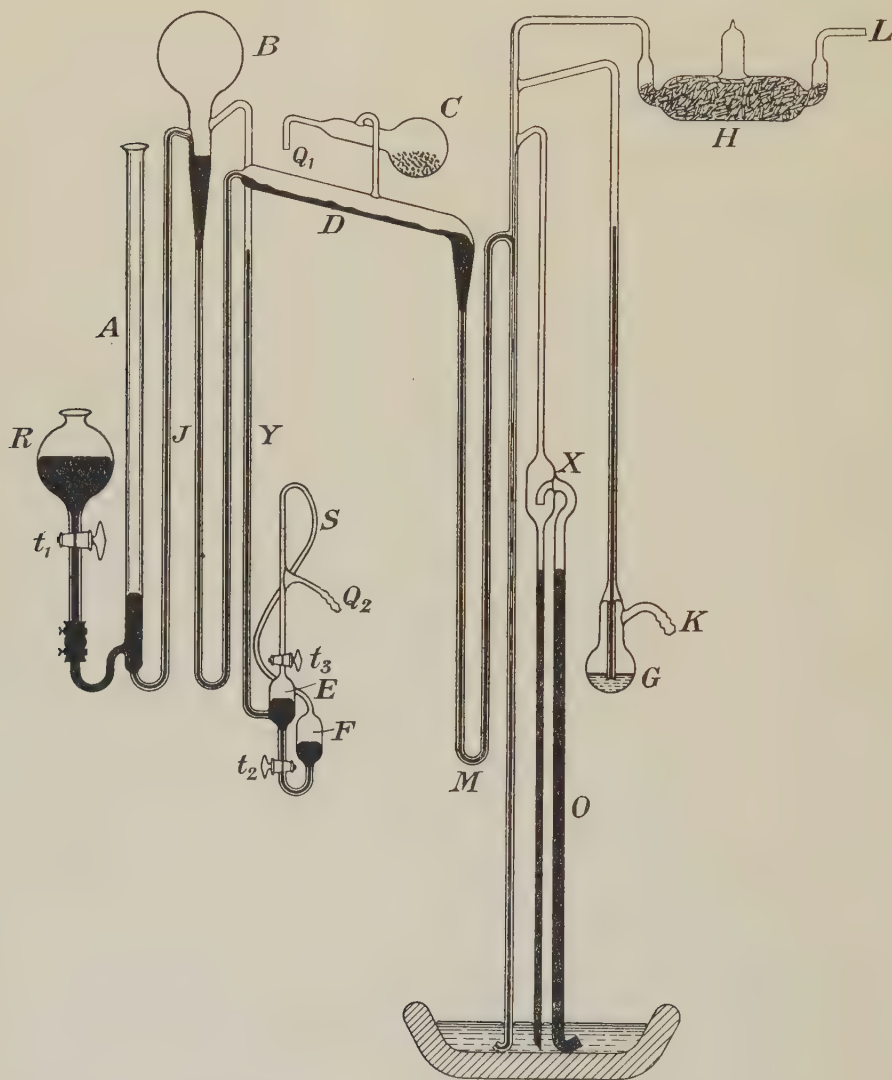


on its way through the apparatus would slowly diffuse into the chamber $C$, and there be absorbed. The large quantity of potash contained in bulb would, however, be but slightly affected.

On admitting mercury from the reservoir $R$, it passes by way of the tube $J$ into the neck of the bulb $B$, whence it falls into the tube below and in so doing loses

accompanying air. Entering the cylindrical chamber $D$ the mercury, in wriggling down the gentle slope, exposes a maximum surface to the high vacuum and is thereby robbed of its last trace of adhering air. As the gas-free mercury flows through the long U-tube $M$, it makes contact with the film of carbon dioxide; and during the action of the pump this film is continuously eroded and so reduced. The detached carbon dioxide is discharged into the fall-tube from whence a little of it is at once carried down and out into the open air the second and by far the greater portion passes backwards towards the vessel that is being exhausted, but on its way thither it is caught and retained by the potash in $H$. Theoretically the efficacy of the pump, when used for the first time, is slightly below its maximum value; but by prolonged action and the consequent erosion of the film upon the walls of $M$, it is raised, step by step, to the highest attainable limit; the greatest power being shown when erosion of the carbon dioxide film ceases and gas is no longer brought into the fall-tube. It will, therefore, be seen that the form and condition of the pump described above secure immunity from certain troubles inseparable from a Sprengel pump of the usual type. In a pump of the ordinary form the air removed by the erosive action of the moving mercury is continuously replaced by other air, and the mass of the film maintained approximately constant. The acquired air appears to be derived partly from that associated with the flowing mercury, but chiefly from the film existing upon the interior of the tube. As to this film the most correct view seems to be that which regards it as a highly attenuated tubular skin; and this when filled with flowing mercury, slides forward but does not terminate; for, although the leading end of the skin on entering the highly exhausted space of the pump is erupted and dispersed, the rearward, having contact with the free atmosphere, is, as it moves on, continuously replenished. Under these conditions even the best pumps of the usual type cannot do more than produce a vacuum in which the pressure is represented by the tension of the advancing and erupting tubular skin. The conclusions here reached are supported by the fact that on using the new pump for the first time, a few gas bubbles appeared at the head of the fall-tube; and that when these had been removed, they were not succeeded by others. Moreover, from that time onward, the efficacy of the pump has, in so far as it has been possible to discover, remained unimpaired.

When, at any time, an appreciable quantity of air has accumulated in $B$, it can be removed by a pump operating at $Q_2$, provided that the approximate use of the stop-cocks $t_2$, $t_3$, is at the same time observed; and this without in the least degree affecting the vacuum in $D$ and $C$.

In conclusion I would draw attention to two very helpful bits of apparatus: these are shown with the pump in the figure.

One is a barometric column of Sprengel pump tubing, to which is fused the cistern $G$; the tube $K$ serves for the attachment of a Geryk, or other pump, whereby the pressure within a vessel sealed to $L$, can be quickly reduced to a small value. As the barometer tube is always closed by mercury, contamination with air from the Geryk pump is avoided. The quantity of mercury in $G$ is such that when the tube is charged, its lower end dips but a little distance beneath the surface. Owing to the small bore of the tube and the wide dimensions of the cistern the level of the mercury is not greatly affected when $G$ is exhausted; hence the effectiveness of the manual pump is a maximum.

The second piece of apparatus $O$, used for the introduction of gases, consists of a twinned barometric column. The tube shown on the right is, for convenience,

I 2

1 cm. wide ; the other may be narrower.   The lower end of the wider tube is bent upward for the reception of gas delivery tubes ;  the upper end is fused to the bulb $X$ within which it terminates as a tapering tube directed downwards.   When a gas enters a vacuum by way of an ordinary barometric column, mercury is thrown upwards so violently that some is frequently carried into narrow connecting tubes ; and these, becoming blocked, are not easily cleared.   This inconvenience is avoided by the use of the twinned column ;  for in this case the mercury that ascends with the gas is, as it enters the bulb $X$, shot downward into the second tube.

### DISCUSSION.

Mr. R. M. ARCHER expressed his interest in the Paper, and thought the use of carbon dioxide, n the manner advocated, a promising departure.   He asked the author which kind of glass he recommended for vacuum work, lead glass or soda glass; also whether he could indicate his experience as to the best method of removal of surface films from metallic vacuum vessels.

Mr. F. E. SMITH remarked that the first person to observe the existence of the surface film on glass was Helmholtz, who demonstrated that a larger quantity of mercury was contained in a tube which had contained paraffin oil than in the same tube when air was previously present, showing that the film of paraffin oil was appreciably less in thickness than that of air.   As illustrating the tenacity with which such surface films persisted, he referred to a Paper read before the Society some 15 years ago, in which it was shown that a film of moisture remained on a glass surface after exposure for some considerable time to a temperature of 500°C.   He thought that the author had made an interesting contribution towards the removal of the difficulties met in high-vacuum work.

Mr. H. P. WARAN said :  It is a matter of common experience to anyone who has used an ordinary Sprengel pump for the production of high vacua that it is on many grounds entirely unsuitable for the purpose in its old form, as employed by the author in the present Paper. Limits of exhaustion as high as ·00001 mm. are rarely realisable in practice in any reasonable length of time when the system exhausted has any appreciable volume.   Generally the pump
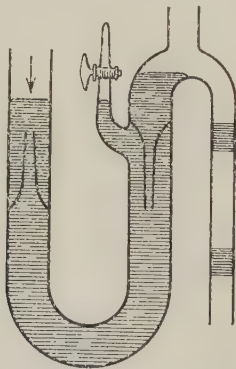


increasingly ceases to function beyond a pressure of the order of ·001 mm. unless the diameter of the fall tube is specially made less than a millimetre, thus considerably prolonging the exhaustion, already very, very slow.   As has already been pointed out by me in an earlier Paper,[*] at pressures of the order of ·001 mm., when the falling pellets begin to hammer, the thin discs of gas formed by the compression in the fall tube get shattered, and find escape back again into the system much easier than downward progress against the barometric column of mercury.

The film of air coming along the walls of the tube, and possibly also traces absorbed by the mercury, have long been known to be sources of trouble in this form of pump and, after the

* Proceedings of the Indian Association, Vol. VI., 199 (1921).

very earliest types, adequately provided for by the provision of vacuum filters on the circuit of the incoming mercury. In my own experience I find a pair of sharp corners as provided by a pair of internal joints in a short U-tube, as indicated on page 90, a simpler and far more effective safeguard to break and check the forward progress of such films, than any number of long bends and complications of the kind. In the modern automatic types of mercury pumps—largely developed in Germany—acting on the Sprengel principle and worked by a filter pump, the vacuum of a few centimetres at the reservoir end considerably reduces the amount of admixed air carried along by the mercury, and the much faster suction of these pumps renders leakages of this order negligible. Further, when the exhaustion is effected by a process of compression, as in the present case, the provision of a large surface of phosphorus pentoxide, located as near as possible to the head of the fall tube, seems to be very essential.

As a further improvement in the details of the type of automatic mercury pump suggested by me some time back, I have evolved recently a simple type of pump of remarkable speed and efficiency, acting on a modified Sprengel principle, and I hope to give publication to its details at an early date.*

From the AUTHOR (communicated) : In reply to Mr. Archer, I may say that I have confined myself to the use of the best soda glass for constructing pumps and apparatus in general. I have no knowledge of the behaviour of lead glass. Although I have made no experiments with metallic vacuum vessels, I should expect marked improvement to follow the use of carbon dioxide for removing other gas skins. The main quantity of the carbon dioxide could be removed by a Geryk pump, and the last portions absorbed by potash previously re-fused.

The Helmholtz experiment described by Mr. Smith is of great interest. With regard to the retention of moisture by glass at a temperature of 500°C., this is in consonance with some preliminary experiments of my own. These show that the complete removal of gas skins from glass surfaces is extremely difficult if not impossible.

In his initial remarks Mr. Waran would appear to have in mind the more elementary forms of the Sprengel pump. With modern forms, provided the tubes are clean, and the mercury frequently purified, there is no difficulty in reducing the pressure within a closed vessel to 0·0002 mm., and that within a reasonable time.

It is, I suppose, common knowledge that at high exhaustions the air discs in the fall tube are shattered by the descending pellets of mercury. Having made a close study of this matter the conclusion I reached was that the shattered discs rarely if ever re-enter the main apparatus. With a fall tube of the usual length there are in general some two or three pellets descending at the same time, and it is difficult to see how the shattered air disc could successfully dodge those, and so return. Mr. Waran's " sharp corners " are really air-traps ; they afford great assistance, more especially when placed just below the head of the fall tube ; the stopcock at *a* is, however, a source of danger, for a slight imperfection would result in a leakage of air into the pump. A tube terminating in a sealed capillary is quite safe.

May I suggest that as the sole function of the phosphoric oxide is the absorption of aqueous vapour, nothing is gained by placing the drying chamber " as near as possible to the head of the fall tube."

* See page 120 of the present volume.

XIII. *On the Measurement of the Radium Content of Sealed Metal Tubes. By* E. A. Owen, *M.A., D.Sc., and* Bertha Naylor, *B.Sc., The National Physical Laboratory.*

### ABSTRACT.

Tables have been compiled giving the corrections that have to be applied to the observed radium content of sealed platinum and silver tubes to obtain their true radium content. Two cases have been considered, namely, (1) that in which the active deposit is uniformly distributed throughout the volume of the tube such as in a full tube of salt, and (2) that in which the active deposit is uniformly distributed over the inner wall of the tube, such as in a tube containing a minute quantity of highly concentrated salt.

The results show that when the wall thickness is kept constant, the correction increases with the external diameter of the tube. Also for the same increase of external diameter, the increase of correction is more pronounced for the "empty" than for the full tube.

RADIUM salts are often sealed in platinum or silver tubes for convenience and safety of application in practice. The measurement of the radium content of such tubes presents a difficulty owing to the uncertainty which exists regarding the correction that has to be applied for the absorption of the radiation in the walls of the tubes. An approximate correction is usually made by measuring the absorption of the radiation in flat sheets of the metal and calculating its value for a thickness equal to that of the wall. This, however, gives only an approximate correction even when the internal diameter of the tube is small, but it may be much in error for tubes of larger diameter. The correction to be applied depends not only upon the thickness of the wall and the diameter of the tube, but also upon the distribution of the active deposit in the tube ; the active deposit may be distributed throughout the whole volume as in a tube filled with salt, or it may be mainly on the walls as in a tube containing a small quantity of highly concentrated salt which occupies only a small amount of space inside the tube.

There is, in addition, the absorption of the radiation in the salt itself which may be considerable for a tube of large diameter.* The correction due to this cause will be omitted here and attention paid only to the corrections arising from the absorption of the radiation in the walls.

The two metals, platinum and silver, will be considered, as they are the metals most frequently met with in this connection.

Two cases arise which can be completely worked out, namely, (1) the case when the tube is full of finely powdered salt and the active deposit may be assumed to be distributed uniformly throughout the whole volume ; and (2) the case when the salt is highly concentrated and the amount of space occupied by it is negligible compared with the internal volume of the tube. In this case the active material will be assumed to be uniformly deposited over the walls of the tube.

In actual practice the majority of cases will be those in which the tubes are only partly filled with salt, so that the correction to be applied to the observed radium content in order to obtain the true content will be intermediate between the results arrived at in the above two cases.

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* *See* Owen and Fage, Proc. Phys. Soc., Vol. XXXIV., Part I., p. 27 (1921).

### (1) *Case of the Full Tube.*

It will be assumed that the tube is situated so far from the measuring chamber that an approximation to a beam of parallel rays is obtained. Let $O$ (Fig. 1) be the axis of the tube placed at right angles to the direction $OC$ which passes through the centre of the surface of the measuring chamber, and let $I$ be the measured intensity
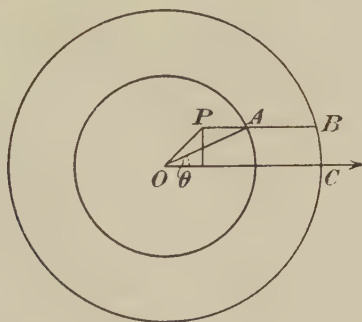


FIG. 1.

of the radiation in the direction $OC$, and $I_0$ the true intensity if there had been no absorption. Consider an element of area $dx\,dy$ at $P$. The intensity of the radiation emitted from this element in the direction $OC$ is

$$\frac{I_0}{\pi a^2} \cdot dx\,dy \cdot e^{-\mu \cdot AB}$$

where

$$AB = \sqrt{b^2 - y^2} - \sqrt{a^2 - y^2}$$

$a$ and $b$ being the internal and external radius of the tube respectively, and $\mu$ the absorption coefficient of the radiation in the metal of the tube. The total intensity of the radiation in the direction $OC$ is, therefore, given by

$$I = \frac{I_0}{\pi a^2} \int_{y=-a}^{y=+a} \int_{x=-\sqrt{a^2-y^2}}^{x=+\sqrt{a^2-y^2}} e^{-\mu\left(\sqrt{b^2-y^2}-\sqrt{a^2-y^2}\right)} \, dy \cdot dx$$

$$= \frac{2I_0}{\pi a^2} \int_{-a}^{+a} \sqrt{a^2 - y^2} \cdot e^{-\mu\left(\sqrt{b^2-y^2}-\sqrt{a^2-y^2}\right)} \, dy$$

Putting $y = a \sin \varphi$, this becomes

$$\frac{I}{I_0} = \frac{2}{\pi} \int_{-\pi/2}^{+\pi/2} \cos^2\varphi \cdot e^{-\mu a\left(\sqrt{(b/a)^2 - \sin^2\phi} - \cos\phi\right)} \cdot d\varphi \quad \cdots \cdots \quad (1)$$

which gives the ratio of the apparent to the true radium content of the tube.

### (2) *Case of the " Empty " Tube.*

In this case the active deposit which emits the hard $\gamma$ radiation whose intensity is measured when estimating the radium content of the tube, is assumed to be entirely distributed over the walls. If $I$ and $I_0$ have the same significance as before, the

intensity of the radiation emitted in the direction $OC$ from a small element of the surface at $A$ is

$$\frac{I_0}{2\pi a} \cdot a \, d\theta \cdot e^{-\mu \cdot AB}$$

where

$$AB = a \left( \sqrt{\left(\frac{b}{a}\right)^2 - \sin^2\theta} - \cos\theta \right)$$

and $\theta$ is the angle which $OA$ makes with $OC$.

Then the total intensity of the radiation in the direction $OC$ is given by

$$I = \frac{I_0}{2\pi a} \int_0^{\pi} a \cdot e^{-\mu \cdot AB} \, d\theta$$

so that

$$\frac{I}{I_0} = \frac{2}{\pi} \int_0^{\pi} e^{-\mu a (\sqrt{(b/a)^2 - \sin^2\theta} - \cos\theta)} \, d\theta \qquad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

The values of the integrals appearing in equations (1) and (2) may be obtained graphically after substituting the proper values for $\mu$.

The measurement of the coefficient of absorption ($\mu$) was carried out on the same apparatus that is employed to standardise samples of radium preparations. This consists of a combined ionisation chamber and electroscope,* the radiation entering the chamber through a lead sheet 5 mm. thick. The source of radiation in the present instance was placed as far as was convenient from the chamber so as to obtain an approximation to a beam of parallel rays. Also the sheets of platinum and silver employed for measuring the absorption coefficient were small—a little larger than that necessary to shield the whole tube from the chamber, the axis of the tube being placed at right angles to the surface of the chamber. In this way the secondary radiation emitted by the absorbing screens was reduced to a minimum. Large sheets would tend to give a value of the absorption coefficient which would be too low on account of the increased amount of scattered radiation superposed upon the primary radiation transmitted by the screen.

The values of the absorption coefficient showed little variation with thickness of screen over the ranges of thickness employed, namely, up to about 0·5 mm. for platinum, and 2·0 mm. for silver. The following mean values were obtained :—

|  | $\mu$ mm.$^{-1}$ |
|---|---|
| Platinum... ...   ...   ... | 0·124 |
| Silver   ...   ...   ...   ... | 0·036$_6$ |

It should be borne in mind that these values apply to radiation emitted by radium in radioactive equilibrium which has passed through 5 mm. of lead before entering the measuring chamber.

The above values of $\mu$ were substituted in the exponentials appearing in equations (1) and (2), and the expressions under the integrals evaluated for different values of $a$ and $b/a$. For each combination of values of these two quantities, a series of values for each expression was obtained for different values of angle, and curves were drawn on a large scale, whose areas were measured by means of a planimeter capable of giving the results to about 1 in 1,000. A summary of the results obtained in this

* Owen and Fage, *loc. cit.*

way are tabulated in Tables I. and II. They give the percentage correction which has to be added to the observed radium content in order to obtain the true radium content of tubes of various external diameters and thickness of wall. For the empty tube no further correction is needed, but for the full tube an additional correction has to be made for the absorption of the radiation in the salt itself.

TABLE I.—*Platinum Tube.*

| External diameter in millimetres. | Full tube. | | | Empty tube. | | |
| | Thickness of wall in millimetres. | | | Thickness of wall in millimetres. | | |
| | 0·3 | 0·4 | 0·5 | 0·3 | 0·4 | 0·5 |
|---|---|---|---|---|---|---|
| 1·5 | 4·3 | 5·3 | 6·6 | 4·9 | 5·9 | 7·0 |
| 2·0 | 4·4 | 5·5 | 6·9 | 5·3 | 6·4 | 7·6 |
| 3·0 | 4·5 | 5·7$_5$ | 7·1$_5$ | 5·7 | 7·1 | 8·3 |
| 4·0 | 4·5$_5$ | 5·9 | 7·3 | 6·0 | 7·4 | 8·8 |
| 5·0 | 4·6 | 5·9$_5$ | 7·4 | 6·2$_5$ | 7·7 | 9·1 |
| 6·0 | 4·6$_5$ | 6·0 | 7·4$_5$ | 6·4$_5$ | 7·9 | 9·4 |
| 8·0 | 4·7 | 6·0$_5$ | 7·5 | 6·7$_5$ | 8·3 | 9·9 |
| 10·0 | 4·7$_5$ | 6·1 | 7·6 | 7·0$_5$ | 8·6 | 10·3 |

TABLE II.—*Silver Tube.*

| External diameter in millimetres. | Full tube. | | | Empty tube. | | |
| | Thickness of wall in millimetres. | | | Thickness of wall in millimetres. | | |
| | 0·5 | 1·0 | 1·5 | 0·5 | 1·0 | 1·5 |
|---|---|---|---|---|---|---|
| 1·5 | 2·0$_5$ | ... | ... | 2·2$_5$ | ... | ... |
| 2·0 | 2·1$_5$ | ... | ... | 2·5 | ... | ... |
| 3·0 | 2·2 | 3·9 | ... | 2·7$_5$ | 4·1$_5$ | ... |
| 4·0 | 2·2 | 4·0$_5$ | 5·8 | 2·9 | 4·5 | 6·1 |
| 5·0 | 2·2$_5$ | 4·1 | 5·0 | 3·0 | 4·7 | 6·5 |
| 6·0 | 2·3 | 4·2 | 6·1 | 3·1 | 4·9 | 6·8 |
| 8·0 | 2·3 | 4·3 | 6·2 | 3·2 | 5·2 | 7·2$_5$ |
| 10·0 | 2·4 | 4·3$_5$ | 6·3 | 3·3$_5$ | 5·5 | 7·6 |

The tables show that when the wall thickness is kept constant, the correction increases with the external diameter of the tube. Also for the same increase of external diameter, the increase of correction is more pronounced for the empty than for the full tube. This is to be expected in view of the nature of the distribution of the active deposit in the two cases.

When the internal diameter approaches zero, it will be noted that equations (1) and (2) both become

$$\frac{I}{I_0} = e^{-\mu b}, \qquad \cdots \cdots \cdots \cdots \quad (3)$$

so that the correction tends towards the value obtained for a flat sheet for both empty

and full tubes as the internal diameter diminishes.  The values of the corrections
when the internal diameter is nearly zero are given in Table III.—

<div align="center">TABLE III.</div>

| | Platinum tube. | | | Silver tube. | | |
|---|---|---|---|---|---|---|
| | Thickness of wall in millimetres. | | | Thickness of wall in millimetres. | | |
| | 0·3 | 0·4 | 0·5 | 0·3 | 1·0 | 1·5 |
| Percentage correction. | $3·6_5$ | $4·8_4$ | $6·0_1$ | $1·8_1$ | $3·6_0$ | $5·3_5$ |

It was of interest to test the above calculations on a few practical cases.  A
glass tube full of radium salt was measured, and found to contain 269·0 milligrammes
of radium element.  This tube was afterwards divided up between six platinum
tubes of 3·0 mm. external diameter and 0·5 mm. thickness of wall.  Each of these
tubes was filled with the salt and hermetically sealed.  After the state of radio-
active equilibrium was reached the tubes were measured, and the total apparent
content was found to be 252·5 milligrammes radium element.  The correction to
be applied to this to obtain the true content, according to Table I. above, is + 7·1
per cent. of the observed content—*i.e.*, 18·0 milligrammes—so that the true radium
content becomes 270·5 milligrammes radium element.  This figure agrees within
about 0·6 per cent. with the radium content of the original tube before it was divided
up.

In another case a glass tube contained 121·6 milligrammes radium element
before being divided up between eleven platinum tubes as follows : Two tubes of
3 mm. external diameter and 0·5 mm. wall ;  three tubes of 2·5 mm. external dia-
meter and 0·5 mm. wall ;  and six tubes of 1·6 mm. external diameter and 0·3 mm.
wall.  The sum total of the contents of these tubes after the appropriate correction
had been added in each case, was found to be 122·5 milligrammes of radium element,
which agrees within about 0·7 per cent. with the radium content of the original
tube.

This agreement is good in view of the possibility of slight loss during sub-division
and the accumulation of small experimental errors in the measurements of the tubes.

The correction for the absorption of the radiation in the salt itself which would
be greater for the original tube than for all the small tubes added together, would
tend to bring the two figures in each case into still closer agreement.

The above two cases suffice to show that the figures given in the above tables
are sufficiently accurate for most practical purposes.

*Note added 7th March, 1922* :—

Table IV. contains the results calculated for tubes of soda glass.  The value
of the absorption coefficient ($\mu$) for soda glass was found to be 0·010 mm.$^{-1}$.  The
figures given in the table, as in the foregoing tables, are the percentage corrections
which have to be added to the observed radium content to obtain the  true radium
content of the tubes.

TABLE IV.—SODA GLASS TUBE.

| External diameter in milli-metres. | Full Tube. | | | Empty Tube. | | |
|---|---|---|---|---|---|---|
| | Thickness of wall in millimetres. | | | Thickness of wall in millimetres. | | |
| | 0·5 | 1·0 | 2·0 | 0·5 | 1·0 | 2·0 |
| .3 | 0·5% | ... | ... | 0·5% | ... | ... |
| 5 | 0·6 | 1·2% | 2·2% | 0·6 | 1·2% | 2·2% |
| 10 | 0·7 | 1·2 | 2·4 | 0·7 | 1·3$_5$ | 2·5 |
| 15 | 0·7 | 1·3 | 2·5 | 0·8 | 1·5 | 2·7 |
| 20 | ... | 1·3 | 2·6 | ... | 1·6 | 2·9 |
| 25 | ... | 1·3 | 2·6 | ... | 1·7 | 3·1 |

DISCUSSION.

Dr. J. S. ANDERSON inquired whether the necessity for a correcting factor might not be avoided by using tubes of rectangular cross-section.

Dr. A. RUSSELL suggested that instead of resorting to a graphical method of integration, use might be made of Weddle's Rule.

Dr. E. A. OWEN, in reply, stated that cylindrical tubes are in common use by the medical profession, as they are easy to handle. Flat applicators are also used, however.

XIV. *The Crystal Structure of Ice.* By Prof. Sir W. H. Bragg, K.B.E., M.A., F.R.S.

### ABSTRACT.

The methods of X-ray analysis have been applied to ice by Ancel St. John and by D. M. Dennison. The former refers the structure to a lattice composed of right triangular prisms of side 4·74 A.U. and height 6·65 A.U. ; the latter to a similar lattice of dimensions 4·52 and 7·32 respectively. The actual arrangement of the atoms is not found in either case.

On certain suppositions, the arrangement can be found independently of direct X-ray analysis in the following way. Let it be assumed that each positive ion is surrounded symmetrically by negative ions, and vice versa ; and in view of the low density of ice, let the number of neighbours be in each case as small as possible. The crystal is to be hexagonal, and is to have the right density. The result is that each oxygen atom is at the centre of gravity of four neighbouring oxygens, from each of which it is separated by a hydrogen atom. The dimensions of the structure agree with Dennison's figures.

The conclusion is supported by a comparison between the calculated intensities of reflection and the observed intensities as recorded by Dennison.

The methods of X-ray analysis have been applied to ice by Ancel St. John[*] and by D. M. Dennison.[†] The two investigators agree in referring the structure to a lattice composed of right triangular prisms of side $a$ and height $c$. St. John gives $a$ and $c$ the values 4·74 A.U. and 6·65 A.U. respectively ; Dennison gives the values 4·52 and 7·32. The complete structure is composed of four such lattices, interpenetrating, and the relative positions of the lattices may be expressed in the following way :—

Let axes of $x$ and $y$ be taken, making an angle of 120° with each other, and the axis of $z$ at right angles to both. The prism $x=0$, $x=a$ : $y=0$, $y=a$ : $z=0$, $z=c$ : contains two of the triangular lattices described above ; each corner of the prism is a point representing a molecule and, therefore, the prism contains the mass of one molecule. According to St. John the three other prisms are derived from the first by parallel shifts, defined by moving the prism corner from 000 to $\frac{a}{3} \cdot \frac{2a}{3} \cdot \frac{c}{n} ; \frac{a}{3} \cdot \frac{2a}{3} \cdot \frac{c}{2} ;$ and $0 \cdot 0 \cdot c\left(\frac{1}{2}+\frac{1}{n}\right)$ in turn. The quantity $n$ is undetermined. Dennison's suggestion is more general. Only two lattices are to be imagined ; and the corners are to be $0 \cdot 0 \cdot 0, \frac{a}{3} \cdot \frac{2a}{3} \cdot \frac{c}{2}.$ *Two* molecules are, however, to be associated with each corner of the prism ; which amounts to saying that the positions of two more lattices are to be derived in the same way by shifting (together) the two that are already defined. St John's definition is, therefore, more particular than Dennison's, but is otherwise in agreement with it. Neither gives a definite value for $n$.

The differences in the values assigned to the constants by the two investigators are rather more than might be expected, especially in view of the care which both seem to have taken.

[*] Proc. Nat. Acad. Sci., p. 193, July (1918).

[†] Science, Sept. 24 (1920) ; Phys. Rev., Jan. (1921).

The values can be shown to give in both cases, as they ought to do, the correct value for the density of ice.

It is interesting to make an attempt to arrive at the structure of ice by an independent method, which, though depending on general information gained by X-ray analysis, does not require special application of the analysis to ice itself.

We assume, as it seems reasonable to do, that ice belongs to the class of crystals in which the molecules are broken into positive and negative ions ; and the structural arrangement is such that each positive surrounds itself with negatives, and each negative with positives. In these crystals the individual molecule is lost. Thus, for example, in sodium chloride or calcium carbonate, the positive (metal) ion is surrounded by six negatives and vice versa. In the case of fluorspar, each calcium atom is surrounded by eight fluorine atoms, each fluorine by four calciums.
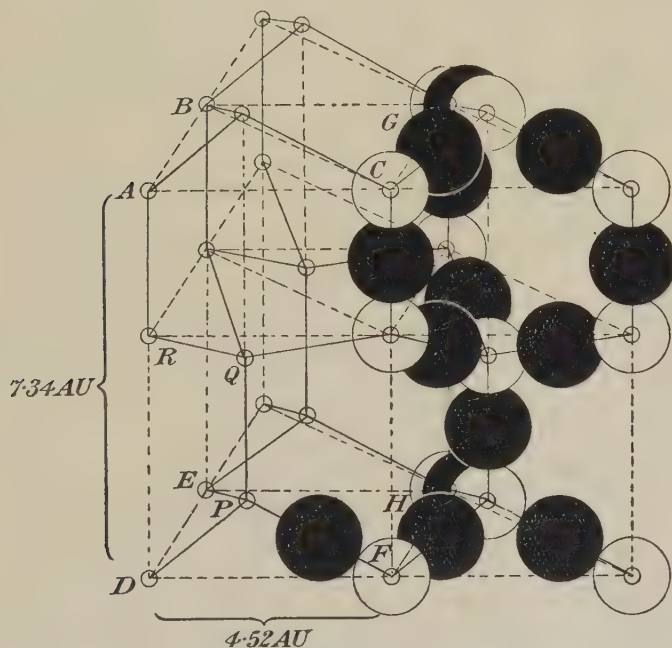


BLACK CIRCLES REPRESENT HYDROGEN ATOMS ; WHITE CIRCLES REPRESENT OXYGEN ATOMS.

In the case of ice we assume that the hydrogens have given up their valency electrons to the oxygens ; and the structure must be such that there are twice as many hydrogens round each oxygen as oxygens round each hydrogen. But the structure must be much more open that that of fluorspar ; a simple calculation shows that if we replace calcium by oxygen and fluorine by hydrogen the distance from the centre of an oxygen to a hydrogen in contact with it must be 2·2 A.U. This is too great : the radius of an oxygen atom in combination with others in crystal structure is in all known cases nearly 0·65 ; we cannot suppose the radius of $H$ to be 1·55 A.U.

The structure must be such that each ion of one sign is closer to its neighbours of the other sign than the fluorspar arrangement allows. The number of atoms in a given volume is limited by consideration of density : if an atom is to be closer to

its neighbours it must have fewer of them. The density of ice is so low, viz., 0·9165, as to suggest that the most economical spacing should be tried. In diamond each atom of carbon has only four neighbours ; the number could not be fewer, if each atom is to be similar in position to all the rest. Diamond is cubic, but there is an alternative structure in which each atom, as in diamond, is at the centre of gravity of its four neighbours, but the crystal is hexagonal. One structure can be obtained from the other by parallel shifts of the (111) planes, without finally altering the value of the universal distance between two neighbours. Zinc oxide is of the latter variety, zinc sulphide of the former.

Let us replace each carbon atom in the hexagonal lattice by oxygen, and insert a hydrogen between each pair of oxygens. Each oxygen is now surrounded by four hydrogens and each hydrogen by two oxygens ; and clearly the number of neighbours has been reduced to a minimum.

The dimensions of the new structure can readily be obtained by comparison with diamond. Each point of the lattice now represents a molecular weight 18 instead of 12, and yet the specific gravity has been lowered from 3·52, the density of diamond or of its alternative arrangement to 0·9165, the density of ice. Hence, if the linear dimensions are increased in the ratio $1 : p$ we have

$$p^3 = \frac{18 \times 3 \cdot 52}{12 \times 0 \cdot 9165}$$

whence
$$p = 1 \cdot 79$$

The distance between the centres of two carbon atoms in diamond is equal to 1·54. Hence the distance between the centres of two oxygen atoms is $1 \cdot 54 \times 1 \cdot 79 = 2 \cdot 76$. The distance between consecutive basal planes is in diamond 2·05 and in the new structure $2 \cdot 05 \times 1 \cdot 79 = 3 \cdot 67$ ; and the distance between two atoms in the same plane is in diamond 2·52 and in the new structure $2 \cdot 52 \times 1 \cdot 79 = 4 \cdot 52$. These figures agree exactly with those of Dennison, because the triangular lattice in terms of which he describes his suggested structure has its base points on three neighbouring atoms in a basal plane, and its height is twice the distance between two (111) planes.

The details of the geometry are shown in the figure. $ABCDEF$ is the right triangular prism the dimensions of which, according to Dennison, are : $AC = 4 \cdot 52$, $AD = 7 \cdot 32$. The prism $x = o$ or $a$, $y = o$ or $a$, $z = o$ or $c$, is the prism $ABCGDEFH$. The four lattices mentioned by St. John are derived from this by shifting $A$ to $P$, $Q$, and $R$ in turn. The value of $n$ is 8.

The structure is extremely empty. It is easy to imagine that a loose arrangement of $H_2O$ molecules would occupy less space, and that pressure would tend to melt the ice. The hydrogen atom has apparently a larger diameter than the oxygen, if we give to oxygen the value 1·30 ; * but it must be remembered that we can only say—assuming the correctness of the structure—that the sum of the diameters of $O$ and $H$ is 2·76 A.U.

The derivation from the hexagonal structure which is the alternative of diamond amounts to assuming that every oxygen atom is at the same distance from each of its four neighbouring oxygen atoms, and that their orientation is regular. The result agrees exactly with the X-ray measurements made by Dennison. In order to get the figures found by St. John it would be necessary to spoil this regularity some-

* W. L. Bragg, Phil. Mag., Aug. (1920).

what ; the substance must be flattened down in the direction of the $z$-axis, and either *PQ* is no longer equal to *PD*, *PE* and *PF*, or the four lines are not regularly oriented about *P*.

Dennison gives in his Paper an estimate of the relative intensities of the different lines based on his photographic results. It is possible to calculate, for the structure given above, the effect—

1. Of the phase differences of the various atoms.

2. Of the relative number of co-operating planes.

The two factors are set out singly and combined in the following table ; and Dennison's estimates are also set out for comparison. In making the calculations it has been assumed that the always expected falling off of intensity with increase of glancing angle ($\theta$) is proportional to the square of the sine of the latter ; this may be only true approximately. The effects of the hydrogen atoms have not been included.

| Plane. | Phase factor. | Number of co-operating planes. | Spacing observed. | Factor proportional to $F.N/\sin^2\theta$. | Observed intensities (Dennison). |
|---|---|---|---|---|---|
| | F. | N. | | | |
| 0001 | 0 | 1 | ... | 0 | 0 |
| 0002 | 8 | 1 | 3·67 | 100 | 100 |
| 0003 | 0 | 1 | ... | 0 | 0 |
| 0004 | 0 | 1 | ... | 0 | 0 |
| | | | | | |
| $10\bar{1}0$ | 4 | 3 | 3·92 | 177 | 10 |
| $20\bar{2}0$ | 4 | 3 | (1·96) | 44 | 0 |
| $30\bar{3}0$ | 16 | 3 | 1·30 | 78 | 2·5 |
| | | | | | |
| $10\bar{1}1$ | 1·76 | 6 | 3·44 | 136 | 20 |
| $10\bar{1}2$ | 2·00 | 6 | 2·68 | 83 | 15 |
| $10\bar{1}3$ | 10·24 | 6 | 2·065 | 243 | 50 |
| $10\bar{1}4$ | 0 | 6 | ... | 0 | 0 |
| $10\bar{1}5$ | 10·24 | 6 | 1·368 | 110 | 20 |
| | | | | | |
| $11\bar{2}0$ | 16·0 | 3 | 2·26 | 236 | 10 |
| $11\bar{2}1$ | 0 | 6 | ... | 0 | 0 |
| $11\bar{2}2$ | 8·0 | 6 | 1·92 | 170 | 10 |
| $1123$ | 0 | 6 | ... | 0 | 0 |
| $11\bar{2}4$ | 0 | 6 | ... | 0 | 0 |
| | | | | | |
| $20\bar{2}3$ | 10·24 | 6 | 1·53 | 143 | 15 |
| | | | | | |
| $20\bar{2}5$ | 10·24 | 6 | 1·167 | 80·0 | 5·0 |

The most striking disagreement is in the large value which Dennison finds for the reflection from the principal plane. Dennison placed a small quantity of distilled water in a thin walled capillary tube of lime glass, which was then plunged quickly into liquid air. Freezing was so rapid that only very minute crystals were formed. The tube was kept at liquid air temperature in a specially-constructed Dewar flask, and rotated continuously during its 10-hour exposure to X-rays. The large (0002) reflection might be due to a tendency to crystallise so that the crystal axis was
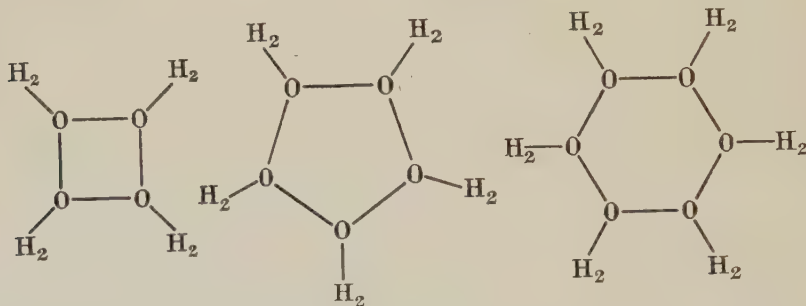
perpendicular to the tube axis. There appears to be a general tendency throughout the table for the planes more nearly at right angles to the (0001) plane to suffer in comparison with the others ; which would point to the same original cause. Dennison records no reflection by $20\bar{2}0$ ; but he records a strong reflection for $11\bar{2}2$, which may really be a compound of the two since the spacings are so nearly the same.

Apart from this, the agreement is really very good. There is, of course, no trace of (0001) itself, nor any (0003) as must be the case for any structure satisfying Dennison's conditions. But, also, there is no (0004), which agrees with the value here given to $n$, viz. 8, and the (0004) should be clear in the experimental results if it really existed because the (0002) is so strong.

I am much indebted to Mr. Shearer for making the calculations set out in the table.

<div align="center">DISCUSSION.</div>

Prof. H. E. ARMSTRONG : The Paper to which we have listened interests me particularly because, as a chemist, I have speculated as to the molecular composition of water, and concluded that a variety of forms are possible. The formula $OH_2$ (hydrone) represents, not water, but dry steam, for in saturated steam such agglomerates as $H_2O$ . $OH_2$ may also be present. No doubt water is saturated with hydrone in a proportion dependent on the temperature, but in addition there may be closed systems containting 4, 5 or 6 oxygens, thus :

$$
\begin{array}{ccc}
\begin{array}{c}
H_2 \qquad\quad H_2 \\
\diagdown \qquad \diagup \\
O \!-\! O \\
| \qquad | \\
O \!-\! O \\
\diagup \qquad \diagdown \\
H_2 \qquad\quad H_2
\end{array}
&
\begin{array}{c}
H_2 \qquad\quad H_2 \\
\diagdown \qquad \diagup \\
O \!-\! O \\
\diagup \qquad\qquad \diagdown \\
H_2\!\!-\!O \qquad\qquad O\!-\!H_2 \\
\diagdown \qquad\qquad \diagup \\
O \\
| \\
H_2
\end{array}
&
\begin{array}{c}
H_2 \qquad\quad H_2 \\
\diagdown \qquad \diagup \\
O \!-\! O \\
\diagup \qquad\qquad \diagdown \\
H_2\!\!-\!O \qquad\qquad O\!-\!H_2 \\
\diagdown \qquad\qquad \diagup \\
O \!-\! O \\
\diagup \qquad \diagdown \\
H_2 \qquad\quad H_2
\end{array}
\end{array}
$$

Now the author's model shows that frozen water contains the potentiality of hexagonal rings of the benzene type. It is remarkable that many substances known to chemists do contain precisely six $H_2O$ units which come and go together. I have here a model constructed of unit spheres to represent a derivative of benzene, the carbon system in which may be taken to represent a slab of water. I assume, however, that the hydrogen atoms occupy half as much space as the oxygen atoms, and that the structure is close-packed. I should like to ask the author whether he could not re-arrange his model in such a way as not to interrupt the continuity of the oxygen chains. At present all the oxygen atoms in it are separated from one another by hydrogen atoms as large as themselves.

It would be interesting if he could also give us some positive information about water in the liquid state, and as to whether a change in structure of the electronic system may not take place at the freezing point. A similar problem arises with regard to various anomalies in the behaviour of metals—for instance, with regard to the atomic heats of metals at very low temperatures. Modern electronic theory may be able to throw some light on these questions.

Dr. A. O. RANKINE : An important feature of the Paper lies in the fact that the space occupied by the hydrogen atom in a crystal has been measured for the first time. It is surprising, in view of the small atomic number of this atom, that it occupies roughly the same space as that of oxygen. It is unfortunate that the X-ray analysis does not indicate the hydrogen planes, but only those of oxygen, because it may be that the layers of hydrogen are not exactly half-way between those of oxygen. My reason for suggesting this is that a hydrogen atom has only one electron to dispose of. If this electron be lent to the oxygen atom on one side of it, there is nothing left for the oxygen atom on the other side. Consequently the binding forces would be different on the two sides, and one would expect uneven spacing.

Dr. F. L. HOPWOOD : It would be interesting to know whether any crystals containing water of crystallisation have been submitted to X-ray analysis. If so, possibly a similar structure may be found in such crystals.

Dr. H. BORNS : With regard to the question raised by the last speaker : Rinne, by the aid of optical tests and Laue radiographs, found that the crystal lattice was not disturbed when the water was expelled by heat from brucite—$Mg(OH)_2$—and in some other cases.

Dr. J. L. HAUGHTON : The anomalous density of water in the neighbourhood of the freezing-point could no doubt be explained if we knew what structural change occurs when water freezes. It is curious that many substances which crystallise in the hexagonal system exhibit such anomalies. Bismuth, for instance, expands on solidifying, and the electrical properties of both bismuth and antimony are correspondingly peculiar at the melting point. Zinc crystallises in the same system, and on solution in acid it gives off less heat if it has been worked than if it has been annealed.

Sir WILLIAM BRAGG, replying to the discussion : The points raised this evening would furnish material for a great deal of research ! The suggestions made by Prof. ARMSTRONG as to the hexagonal ring in water are intensely interesting. The method tells us nothing about the liquid, and nothing therefore about the structural change at the freezing-point, but it is quite clear that the structure is *not* close-packed, and that the unit in the crystal is the atom, not the molecule. It cannot be said that a given hydrogen atom belongs to one oxygen atom more than another. The oxygens are entirely separated by hydrogens : it is a striking feature, so far, of the models of polar crystals that the positives touch negatives only and *vice versa* ; exceptions to this rule occur, but they seem to be accidental and due to some special cause. For instance, the *Al* atoms in ruby touch each other, but they are driven into contact.

On the question raised by Dr. Rankine as to whether the hydrogen atoms are located half-way between the oxygen atoms, we have no guide except symmetry. If I move a given hydrogen atom nearer to a given oxygen atom, I shall be obliged to move a corresponding hydrogen atom in the opposite direction, and there will be a loss of symmetry.

In reply to Dr. HOPWOOD, some alums, which contain water of crystallisation, have been investigated.

XV.  *A Method of Exciting Vibrations in Plates, Membranes, etc., Based on the Bernoulli Principle.*  By PROF. KERR GRANT, *University of Adelaide.*

RECEIVED JANUARY 1, 1922.

(COMMUNICATED BY SIR W. H. BRAGG, F.R.S.)

ABSTRACT.

It is known that a plate placed close to a flanged orifice from which a stream of air or liquid is issuing is attracted towards the orifice.  If the plate be mounted as a diaphragm it can be excited to strong vibration by a suitable blast, and a loud sound is produced with high efficiency.

THE apparent attraction which is exerted between two closely juxtaposed surfaces when a stream of air flows between them is well known.  Witness, for example, the experiment of lifting a light object, such as a matchbox, by blowing through a pipe, provided with a flange placed in loose contact with the surface of the object.

It occurred to the writer in 1918 that this effect might be applied to maintain vibrations in a plate or diaphragm, since the vibratory motion of the plate or
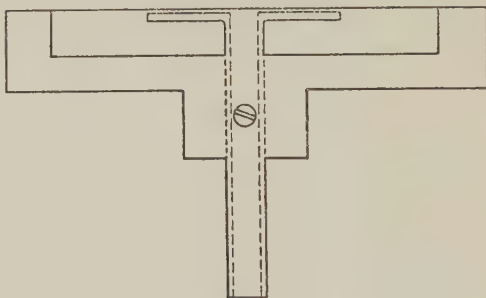


FIG. 1.

diaphragm could operate as a valve to stop or permit the flow of air, and thus give the variations of pressure necessary to maintain the vibrations.  (For brevity any sound-producing appliance based on this principle will be termed a hooter.)

To test this idea a piece of parchment was mounted on a circular wooden ring about 5 in. in diameter and a three-eighths inch brass pipe provided with a flange of brass-plate about 2 in. in diameter, mounted in such a way that the surface of the flange could be adjusted parallel with and in the closest proximity to the parchment diaphragm (Fig. 1).  When the pipe was supplied with air from a compressor the parchment was excited to vigorous vibration with the production of a very intense sound, the pitch of which varied with the pressure of the air supplied and the degree of approximation of the flange to the parchment.  In general overtones were produced, but by operating at lower pressures and by careful adjustment the diaphragm could be made to vibrate in its fundamental mode.

A pressure of a few pounds to the square inch was found to be sufficient to maintain vibration.  In fact, a powerful sound can be obtained by using this appliance as a trumpet.

When a plate of thin sheet-metal was substituted for the parchment somewhat higher pressures were found to be necessary for excitation, the pressure requisite depending, as might be expected, on the stiffness of the plate.

With diaphragms of sheet-metal which are so thick as to function as plates rather than as membranes and yet not thick enough to permit of being accurately machined there is some difficulty in putting on the diaphragm in such a way as to secure a good approximation to a plane. A fairly satisfactory method of doing this is to leave a slight rim on the inner periphery of the supporting ring and then screw down the holding-down ring while the diaphragm is kept hot by a hot metal plate laid upon it. The plate then approximates very nearly to a true plane except for a short distance inwards from its periphery. If it is not expanded during the process of screwing down, the surface takes a hemispherical form. Fig. 2 illustrates the construction of a sheet-metal hooter on the above lines.

A metal hooter was found to operate successfully when the water in the supply main, at a pressure of about 80 lbs. per square inch, was substituted for air as the driving agent. The hooter operated in this case whether it were held in the air or immersed in water.
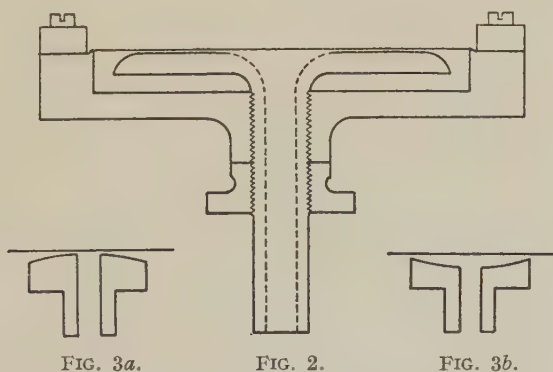


FIG. 3*a*.  FIG. 2.  FIG. 3*b*.

While the author was engaged during the summer of 1919 at the Research Laboratory of the General Electric Co., Schenectady, N.Y., several hooters were, by the courtesy of the Director, constructed, the largest having a plate of sheet-iron about 1 ft. in diameter and one-eighth inch in thickness. This operated very well on a compressed air supply at a pressure of 80 lbs. per square inch, and could probably be heard under favourable conditions at a distance of one mile. There seems no reason why hooters of very much larger dimensions should not function equally well or better, in which case a sound production of intensity comparable with those of the most powerful sirens or whistles might be expected.

A rough comparison as regards efficiency of sound-production was made between this large hooter and the standard type of compressed-air whistle used on the Schenectady Electric Cars. The sound of this whistle on full air-consumption was appreciably louder than that of the hooter, but since it required for this a 1-inch supply-pipe as against the three-eighths inch on the hooter, it would appear that the latter is very much more efficient.

The efficiency of the hooter as a sound-producer depends in a high degree upon the details of its construction. One condition for good operation is that the

mass of the flanged pipe, together with that of the frame in which it is rigidly supported, should be large compared to that of the vibrating plate or membrane. If this is not so the flange will also vibrate and not only waste energy but interfere with the vibration of the diaphragm.

The amount of air used depends also very largely on the closeness with which the flange can be approximated to the plate—actual contact does not prevent operation—and on the nearness with which exact parallelism of the two surfaces is attained.

The more massive the vibrating plate the better is the adjustment necessary in these respects for satisfactory operation, and for large hooters it is likely that both exact geometrical form and polishing of the juxtaposed surfaces would be desirable.

It is an advantage to vary the surface of the flange from a true plane to a form slightly convex towards the plate and to expand the end of the pipe, as shown in Fig. 3*a*. Probably the space between vibrating plate and flange should vary in sectional area according to the principle of the Venturi-nozzle. If, on the other, the departure from a true plane is in the direction of concavity towards plate or diaphragm (Fig. 3*b*), the operation of the hooter is adversely affected even to the point of failure.

No absolute measurements of the efficiency of the hooter as a sound-producer have yet been made. The comparison with the whistle alluded to above, and the very striking reduction in the quantity of water issuing between flange and plate, which takes place as soon as the latter commences to vibrate, would indicate that this is of a fairly high order.

No attempt at exact mathematical treatment of the energy and force relations involved in the action of this hooter will be made in this paper. Qualitatively the theory of operation is no doubt somewhat as follows : Let the plate be initially at rest with no fluid flowing. The static pressure of the fluid in the supply pipe produces a displacement of the plate or membrane calling into play an opposing force due to elastic resistance or tension, as it may be. Fluid now flows between plate and flange reducing the pressure and permitting return of the plate or membrane up to and beyond its equilibrium position. The flow is thus nearly or completely stopped with consequent rise of pressure up to and beyond the static pressure in the supply system ; the plate is then driven back by this pressure and the cycle repeated.

During the first stage work is done by the plate upon the fluid in the supply pipe ; during the second, positive work is done by the fluid upon the plate. Since the average pressure is clearly higher during the second stage, the total work done by the fluid on the plate in a cycle is positive.

The production of the sound is due no doubt mainly to the vibrations of the plate or membrane itself, but also in some degree upon the siren-effect of the intermittent outflow of air. This is put in evidence by the fact that the sound is emitted most strongly, at least for some hooters that have been tried, on the side of the nozzle. It might, therefore, be an improvement to modify the construction in such a way as to cause the escaping air to issue in front instead of, as at present, behind the plate.

The frequency of the note depends, of course, mainly on the natural period of the plate or membrane ; but this is probably modified in the case of a membrane very considerably, in the first place, by the pressure of the driving fluid,

which will, of course, cause variations of tension in the membrane, and, secondly, by the very heavy damping due to the air-cushion between flange and plate. The presence of this air-cushion probably accounts for the fact that a hooter will vibrate freely even when the flange is actually in contact with the plate or membrane before vibration commences. The damping is sufficient for all hooters yet experimented with to cause instant cessation of the sound when the supply is cut off. An easy method of varying the frequency of a given plate is to load it centrally with different masses tightly screwed or soldered on.

It is probable that frequencies well above the limit of audibility could be obtained, though no hooter has yet been made to test this point. An application to the purposes of submarine signalling suggests itself. For this steel plates comparable with those used in the Fessenden oscillator would be necessary. An auxiliary high pressure water pump with a suitable rapid action control valve would be the only accessories required. The radiation of high frequency waves from an area large compared to the wave length is, as is well known, highly directive in character. In fact, the addition of a horn to the large hooter described above, the frequency of which was certainly below 1,000 d.v. per sec., made very little increase in the amount of sound radiated along the axis of the plate.

I have to thank Mr. A. L. Rogers, mechanic to the Physics Department, for giving the benefit of his skill and experience to the construction of the hooters made and tested here.

### DISCUSSION.

Dr. F. L. Hopwood remarked that the ingenious device which had been described afforded an instance of the solution of a new problem by the inversion of an old one. It might be advantageous to provide the instrument with a resonator.

XVI. *The Number of Radio-active Transformations as Determined by Analysis of the Observations.* By H. LEVY, M.A., D.Sc. (*Asst. Professor of Mathematics, Imperial College of Science*).

## ABSTRACT.

It is known that the expression for the $n$th product of a series of radio-active transformations is properly represented as the sum of $n$ terms of the type $a_n e^{-\lambda_n t}$. When $n$ is known, the coefficients $a_n$ and $\lambda_n$ are determinable with comparative ease. The present Paper finds a criterion for determining $n$, the number of transformations, when this is not known from *a priori* considerations. This consists in the successive evaluation of a system of simple determinants easily constructed from the observations. The value of $n$ is at once found from the order of the particular member of the system that vanishes.

IN a Paper " On the Resolution of a Curve into a Number of Exponential Components,"[*] Mr. J. W. T. Walsh has developed a method for the determination of the coefficients $a_r$ and $\lambda_r$ in the expression for the amount of the $n$th product $N(t)$ in a series of successive transformations, where

$$N(t) = a_1 e^{-\lambda_1 t} + a_2 e^{-\lambda_2 t} + \ldots \quad + a_n e^{-\lambda_n t} \quad \ldots \ldots \ldots (1)$$

In the subsequent discussion on the above Paper it was urged that a crucial difficulty in the application of the analysis to any particular case was the lack of knowledge with regard to the actual number $n$ of the transformations which occurred, unless this deficiency could be made up from a priori considerations. Unless the appropriate number of terms were adopted in the expression for $N(t)$, it seemed obvious that wrong values would be found for the coefficients $a$ and $\lambda$. As stated in the Paper referred to, the method there adopted was analogous to the Lagrange-Dale method of analysis of periodic observations.

In actual fact, a still closer analogy with the latter method enables the number $n$ of transformations to be easily determined, and indicates the effect that would be produced on the coefficients if a wrong number were selected. The present Paper deals principally with these two points.

Let $N_0, N_1, \ldots N_r \ldots$ be a series of observations of the products of radio-active transformations corresponding to times $t = 0, 1, \ldots r \ldots$, or a series of values taken from a smoothed curve of such observations for equidistant values of the time interval if the observations were not actually recorded at these times. The unit of time adopted may for the moment be supposed so selected as to provide from the experimental curve any desired number of values $N_0$, $N_1$, &c. When there are $n$ successive radio-active transformations, I assume $N$ can be expressed in the form (1). In effect, the problem is to determine $n$ and the $2n$ constants $a_1 \ldots a_n, \lambda_1 \ldots \lambda_n$.

Following the method adopted in the Paper referred to, except that we do not restrict ourselves only to $2n$ observations, let

$$x_1 = e^{-\lambda_1}, \quad x_2 = e^{-\lambda_2}, \quad \ldots \quad x_n = e^{-\lambda_n}$$

[*] Proc. Phys. Soc., Vol. XXXII., p. 26.

Then the $\lambda$'s will be determined when the $x$'s are obtained. Expression (1) now becomes

$$N_t = a_1 x_1{}^t + a_2 x_2{}^t + \ldots + a_n x_n{}^t \qquad \ldots \ldots \ldots \quad (2)$$

The observations $N_0$, $N_1$, etc., corresponding to the successive times $t=0$, 1, . . $r$ . . . must accordingly satisfy the following relations

$$
\left.
\begin{array}{l}
N_0 = a_1 \quad + a_2 \quad + \ldots \quad + a_n \\
N_1 = a_1 x_1 + a_2 x_2 + \ldots \quad + a_n x_n \\
\cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \\
N_r = a_1 x_1{}^r + a_2 x_2{}^r + \ldots \quad + a_n x_n{}^r \\
\cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot
\end{array}
\right\} \quad \ldots \ldots \ldots \quad (3)
$$

The system (3) will consist of as many equations as we care, by taking the same number of values of $N$ from the experimental curve. If we choose $2n$ such values, we shall have just sufficient equations to determine the $2n$ constants $a_1$, $a_2$, etc., and $x_1$, $x_2$ . . . etc. If we choose more than $2n$ values of $N$, the system (3) will only be consistent if certain relations hold among the known values of $N$. These latter relations are in effect the conditions that must be satisfied if the additional values of $N$ are to lie on the curve (1), as determined by the first $2n$ observations. These conditions, it will shortly be seen, enable us quite simply to determine $n$, the number of terms in (1).

Let the $n$ quantities $x_1$, $x_2$ . . . $x_n$ be roots of the equation

$$x^n + p_1 x^{n-1} + \ldots + p_{n-1} x + p_n = 0 \qquad \ldots \ldots \ldots \quad (4)$$

Consider the expression

$$S(n,r) = N_{n+r} + p_1 N_{n+r-1} + p_2 N_{n+r-2} \ldots + p_n N_r \qquad \ldots \ldots \quad (5)$$

where $r$ is any positive integer. Inserting the expressions for the $N$'s from (3)

$$S(n, r) = \sum_{s=1}^{s=n} a_s x_s{}^{n+r} + p_1 \sum_{s=1}^{s=n} a_s x_s{}^{n+r-1} + \ldots + p_n \sum_{s=1}^{s=n} a_s x_s{}^r$$

$$= \sum_{s=1}^{s=n} a_s x_s{}^r [x_s{}^n + p_1 x_s{}^{n-1} + \ldots + p_n]$$

$$= 0$$

in virtue of the fact that $x_s (s=1, \ldots n)$ is a root of (4). Accordingly, we can have as many expressions of the type (5) equated to zero as our observations will allow.

Corresponding to successive values of $r=0$, 1, . . . the following system of relations between the observations must be satisfied

$$
\left.
\begin{array}{l}
N_n \quad + p_1 N_{n-1} \quad + p_2 N_{n-2} + \ldots \quad + p_n N_0 = 0 \\
N_{n+1} + p_1 N_n \quad + p_2 N_{n-1} + \ldots \quad + p_n N_1 = 0 \\
\cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \\
N_{n+r} + p_1 N_{n+r-1} + p_2 N_{n+r-2} + \ldots \quad + p_n N_r = 0 \\
\cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot
\end{array}
\right\} \quad \ldots \quad (6)
$$

By selecting any arbitrary block of $(n+1)$ of these equations we are enabled to eliminate the unknown coefficients $p_1 \ldots p_n$, deriving a whole system of determinants, each of which must vanish, and restricted in number only by the number of observations available. These determinantal equations are simply the condition

that the observed values of $N$ shall consistently correspond to points which fall on the curve defined by (1). The constants in (1) are, moreover, determined by associating with (4) any $n$ equations of (6), and again eliminating $p_1 \ldots p_n$ when a series of determinantal equations, of which the following is a simple type, will be obtained :—

$$
\begin{vmatrix}
x^n, & x^{n-1}, & \ldots & & x, & 1 \\
N_n, & & & \ldots & N_1, & N_0 \\
\cdot & & & & & \cdot \\
\cdot & & & & & \cdot \\
\cdot & & & & & \cdot \\
\cdot & & & & & \cdot \\
\cdot & & & & & \cdot \\
N_{n-1}, & & \cdot & \ldots & N_n, & N_{n-1}
\end{vmatrix} = 0 \quad \ldots \ldots \quad (7)
$$

This is the equation obtained by Mr. Walsh for the various values of $x$, but, of course, it is only one of a whole series of such equations. If the observations were exact, and if $n$ be correctly chosen these equations must all be identical, but in practice they will differ. As in the Lagrange-Dale method for periodic analysis, the equations of type (7) enable us to replace them by one of similar form to (7), embodying all the observations. The single observations are there replaced by the sum of groups of observations. I do not propose to develop this here, however.

The vanishing of the determinants formed by eliminating $p_1 \ldots p_n$ from any $n+1$ equations of the system (6) obviously provides us with the criterion for the determination of $n$, for the observations are merely set down in a series of symmetrical determinants of $n+1$ rows and columns of the form

$$
\begin{vmatrix}
N_n, & N_{n-1}, & \cdot & \cdot & \cdot & \cdot & \cdot & N_0 \\
N_{n+1}, & & \cdot & \cdot & \cdot & \cdot & \cdot & N_1 \\
\cdot & \cdot & & & & & \cdot & \\
N_{2n-1}, & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & N_{n-1} \\
N_{2n}, & & \cdot & \cdot & \cdot & \cdot & \cdot & N_n
\end{vmatrix} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (8)
$$

for successive values of $n = 1, 2, 3, \ldots$ , until for some value of $n$ the determinant in question vanishes. It cannot moreover vanish for $n$ less than the correct value, for otherwise this would imply that the points corresponding to the observations could lie on a curve for which $n$ is less than the correct value. Every such determinant formed by taking $n$ greater than the correct value will also vanish since all the minors are zero. The query was raised in the discussion on Mr. Walsh's Paper, whether, if too many terms are assumed in (1), say, by the addition of a term $a_{n+1}e^{-\lambda_{n+1}t}$ when there have been only $n$ radio-active transformations, all the constants will readjust themselves in value. In the event of such an error, however, since all the determinants of which (8) is a simple type must vanish, all the minors of the new determinantal equation (7)—an equation now of degree $n+1$ in $x$—will consequently vanish and the coefficients of the various powers of $x$ in (7) will all be zero ; or at any rate, in practice their values will be due to observational errors.

We have thus established a complete criterion for the determination of the number of radio-active transformations. In any particular case since the values of $N$ are subject to experimental errors the determinant (8) will not vanish exactly and it becomes necessary to compare the magnitudes of the successive determinants. For a legitimate comparison, therefore, it is advisable to reduce the observations

taking, say, $N_0$ as unity, *i.e.*, by dividing each observation by $N_0$, otherwise the effect of the errors may increase in absolute amount with increase in order of determinants.

While for a determinant of any particular order it is a comparatively simple matter to find an expression for the effect on the value of the determinant of small observational errors in the quantities $N_t$, I have been unable to find a simple expression from which the effect of such errors in general may be directly estimated. Where there is a systematic proportional error, that is, where instead of the accurate value $N_t$, the erroneous value $N_t(1+a)$ occurs where $a$ is a small constant, it is evident that the process of dividing each observation by $N_0(1+a)$ before constructing the determinant will completely eliminate any error from the value of the determinant. If again the observational error increases with the value of $t$ so that, say, instead of the accurate value $N$ the erroneous value $N_t(1+ta)$, or $N_t(1+a)^t$ is observed, where $a$ is a small constant, the vanishing of the determinant is likewise not affected ; for determinant (8) becomes—writing down merely the diagonal terms :

$$\mid N_0, N_2(1+a)^2, N_4(1+a)^4, \ldots \ldots N_{2n}(1+a)^{2n} \mid \; = (1+a)^{n(n+1)} \mid N_0, N_2, \ldots N_{2n} \mid$$

It follows that the error in the estimation of a determinant of $n+1$ rows and columns is approximately $n(n+1)a$ times the value of the determinant, and, therefore, vanishes with the determinant. These two cases seem to suggest that no serious difficulty is to be anticipated on these grounds.

As an illustration we may take the example given in Mr. Walsh's Paper, where the author assumes or knows from *a priori* considerations that only two terms of the type (1) are present. Plotting the given observations on a smooth curve I derive the following data, by interpolation where necessary :—

| $t$ | = | 0 | 1 | 2 | 3 | 4 | 5 | 6 . . . . |
|---|---|---|---|---|---|---|---|---|
| $N$ | = | 278 | 142 | 107 | 84 | 70 | 59 | 50 . . . . |
| $N_t/N_0 = N_t' =$ | | 1 | 0·512 | 0·385 | 0·302 | 0·252 | 0·212 | 0·180 . . . . |

$$\therefore \quad \begin{vmatrix} N'_1, & N'_0 \\ N'_2, & N'_1 \end{vmatrix} = \begin{vmatrix} ·512, & 1 \\ ·385, & ·512 \end{vmatrix} = -0·123$$

$$\therefore \quad \begin{vmatrix} N'_2, N'_1, N'_0 \\ N'_3, N'_2, N'_1 \\ N'_4, N'_3, N'_2 \end{vmatrix} = \begin{vmatrix} ·385, ·512, & 1 \\ ·302, ·385, & ·512 \\ ·252, ·302, & ·385 \end{vmatrix} = -0·002$$

$$\therefore \quad \begin{vmatrix} N'_3, N'_2, N'_1, N'_0 \\ \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \\ \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \\ \cdot \; \cdot \; \cdot \; \cdot \; \cdot \end{vmatrix} = \&c. \quad \ldots \ldots = 0·000007$$

Since the data are scarcely correct to the third figure and the above calculations have been carried through on a simple slide-rule, we may conclude that the determinants of third and higher orders vanish ; it follows that there must be two terms in the appropriate expression (1).

## DISCUSSION.

Mr. T. SMITH said that the method of finding the number of terms described by Prof. LEVY placed the analysis of observations of this type on a satisfactory basis. He wished to suggest that the absolute magnitude of the determinants used as an illustration by the author did not provide the key to the number of terms which should be considered, but rather the relative magnitude of successive determinants should be taken. In the preliminary examination to find $n$, it would be convenient to adopt as the unit for the $N$'s the probable error due to experiment and graphical interpolation combined. The successive determinants will then at first rise, come to a stationary value, and afterwards fall. The number of determinants on the rising portion of the series would indicate the number of terms justified by the observations. For instance, if in the original example the total error is not likely to exceed $\pm 1$ in any observation, the values of successive determinants arranged with the extreme readings on the main diagonal are

$$278, \quad 9582, \quad 36721, \quad -2344,$$

showing that the observations require the presence of three terms. If on the other hand the individual errors may amount to $\pm 4$, the values of the same determinants may be written approximately as

$$4 \times 70, \quad 4^2 \times 600, \quad 4^3 \times 570,$$

so that the evidence for the inclusion of a third term is inconclusive. The observations themselves show that, if the assumed mathematical form is applicable to them, the accuracy in this case is not as great as $\pm 4$, since the solution when three terms are assumed to exist involves a harmonic component in one of them, and the character of the phenomena observed may be assumed to exclude the reality of such a factor.

A preliminary analysis by means of differences of increasing orders appears to be valuable when the observations are thought to be consistent with laws of this class. In the present example from the series

$$278, \ 142, \ 107, \ 84, \ 70, \ 59, \ 50, \ \ldots$$

the leading differences are

$$278, \ 136, \ 101, \ 89, \ 86, \ 89, \ 97 \ \ldots$$

and the tendency to increase without changes of sign after a certain point indicates the presence of a term alternating in sign in successive observations. Corresponding to the original observations

$$N_0 = a_1 + a_2 + a_3 + \ldots$$
$$N_1 = a_1 x_1 + a_2 x_2 + a_3 x_3 + \ldots$$
$$\cdot \qquad \cdot \qquad \cdot \qquad \cdot$$
$$N_r = a_1 x_1{}^r + a_2 x_2{}^r + a_3 x_3{}^r + \ldots$$

we have the successive differences

$$D_0 = a_1 + a_2 + a_3 + \ldots$$
$$D_1 = a_1 y_1 + a_2 y_2 + a_3 y_3 + \ldots$$
$$\cdot \qquad \cdot \qquad \cdot \qquad \cdot$$
$$D_r = a_1 y_1{}^r + a_2 y_2{}^r + a_3 y_3{}^r + \ldots$$

where
$$x_1 + y_1 = x_2 + y_2 = x_3 + y_3 = 1,$$

showing that the differences form a series of the same type as the original series. This formula indicates that if after some point the $D$'s increase in magnitude without change of sign at least one of the $y$'s is greater than unity—that is, at least one of the $x$'s is negative. The analysis can evidently be carried out on the differences just as well as on the original figures. In complicated cases it appears desirable to determine short period terms from the original figures, and after these are removed to calculate long period effects from the differences for the remainder.

Mr. J. W. T. WALSH (communicated remarks): The criterion which Dr. Levy has found for determining the number of the terms in a composite exponential curve will be of great value to those who have to analyse such curves without any *a priori* guide to the number of terms present.

The principal difficulty in the practical application of the method is, of course, the presence of the unavoidable errors of observation, and the magnitude of these may be such as to make the verdict of the criterion somewhat uncertain, especially if two of the components really present happen to have values for the exponent which only differ by a comparatively small quantity.

It seems difficult to imagine a method which will avoid this difficulty, and probably the only course to adopt in such a case is to determine the constants for $n$ components, where $n$ is the smallest value indicated by the application of the criterion. If the differences between the observed values and the values thus calculated for $n$ components do not in any case much exceed the estimated experimental error, then $n$ must presumably be adopted as correctly representing the observations to experimental accuracy. If, however, the differences somewhat exceed the experimental error, then a further component may justifiably be included.

The AUTHOR, in reply, stated that Mr. Walsh's analysis had been developed from a method given by Dr. Dale, and applicable to periodic functions (indices of exponential terms imaginary). The extension given by Mr. T. Smith was analogous to a further procedure indicated by Dr. Dale, and, like the latter, had the advantage that the experimental errors of a plurality of terms were averaged, whereas without such procedure undue effect would be given to the errors of individual observations. Dr. Dale had shown that sums and differences of blocks of observations could be employed in the place of individual observations. Undoubtedly, the method indicated by Mr. Smith was the correct one for determining the required constants.

XVII. *On a Graphical Method of Treating Fresnel's Formulæ for Reflection in Transparent Media.* By CHARLES H. LEES, D.Sc., F.R.S.

ABSTRACT.

It is shown that Fresnel's Formulæ for Reflection in Transparent Media may be treated by a simple graphical method which allows the effects of variations of the angle of incidence and of the refractive indices of the media to be traced readily.

(1.)

IN tracing the variations of the amplitude of the reflected wave $R'$, when an electromagnetic wave $I$ is incident at different angles on a surface separating two media transparent to the wave, I have found that a graphical method appeals more readily to students than an analytical treatment of the two well-known Fresnel expressions

$$\frac{R'}{I} = \frac{\tan{(r-i)}}{\tan{(r+i)}}$$

when the electric vector is in the plane of incidence, and

$$\frac{R'}{I} = \frac{\sin{(r-i)}}{\sin{(r+i)}}$$

when it is normal to that plane, $i$ and $r$ being the angles of incidence and of refraction respectively.

As it is possible that others have had a similar experience, I reproduce here the graphical method I have found most convenient, in order that its suitability may be tested by a wider circle.

(2.)

In the figures which follow, $IP$ is the incident, $PR'$ the reflected and $PR_1$ the refracted ray,* $\mu$ the index of the first and $\mu_1$ that of the second medium. The incident $IP$ and reflected $PR'$ rays are produced beyond the surface if necessary. The distance $PI$ is set off along the incident ray equal on some convenient scale to the component, either in or perpendicular to the plane of incidence, of the amplitude of the electric oscillation in the incident ray.

Through $I$, $IQ'$ is drawn parallel to the refracted ray $PR_1$, cutting the reflected ray $PR'$ or the ray produced in $Q'$. When $PI$ represents the component perpendicular to the plane of incidence of the amplitude of the electric oscillation in the incident ray, $PQ'$ represents on the same scale the amplitude of the electric oscillation perpendicular to the plane of incidence in the reflected ray, since the angle $PIQ'$ is $i \sim r$ and the angle $PQ'I$ is $i+r$, and the sides of the triangle $IPQ'$ are as the sines of the opposite angles.

Through $Q'$, $Q'Q$ is drawn perpendicular to $IQ'$, to cut the incident ray $IP$ or the ray produced in $Q$. When $PI$ represents the component in the plane of incidence of the amplitude of the electric oscillation in the incident ray, $PQ$ represents on the

---

* In Figs. 1 and 4 the refracted ray is not shown in order to avoid confusion.

same scale the amplitude of the electric oscillation in the plane of incidence in the reflected ray, since if a perpendicular $PP'$ were drawn from $P$ on to $IQ'$,

$$QP/PI = Q'P'/P'I = \cot(i+r)/\cot(i \sim r).$$

As it is a convenience to represent the amplitude of the electric oscillation in a given ray by a length measured along that ray, $QS'$ is drawn through $Q$ parallel to the reflecting surface at the point of incidence, cutting the reflected ray $PR'$ or the ray produced in $S'$. Thus, $PS'$ represents the amplitude of the electric oscillation in the plane of incidence in the reflected ray.

In order to distinguish in the figures the two directions of oscillation, dots have been placed alongside the line representing the amplitude of an oscillation perpendicular to the plane of incidence, and short lines alongside and at right angles to the line representing the amplitude of an oscillation in the plane of incidence.
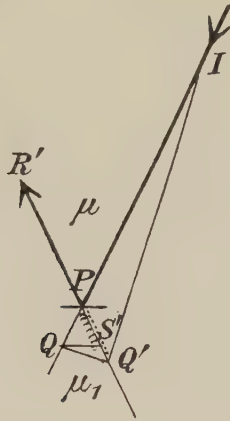


FIG. 1.—INCIDENT AMPLITUDE $PI$, REFLECTED $PQ'$ AND $PS'$.

When the amplitude is shown as a line measured from the point of incidence $P$ along the reflected ray $PR'$ it indicates that there is no reversal of the oscillation, or, what is equivalent, no loss of half a wave length, on reflection. When the amplitude in the reflected ray is shown as a line measured from $P$ along the reflected ray produced backwards, it indicates reversal of the oscillation or loss of half a wavelength on reflection.

If the electric oscillation is neither in nor perpendicular to the plane of incidence, it is resolved into its components in these two directions, the reflected oscillations $PQ'$ and $PS'$ due to them are determined by the construction and the resultant of the two is then $\sqrt{PQ'^2 + PS'^2}$.

If, as in the case of ordinary light, the electric oscillation is equally in all directions perpendicular to the incident ray, the mean reflected amplitude is still $\sqrt{PQ'^2 + PS'^2}$, if $PI$ is the mean incident amplitude.

(3.)

The most important facts connected with the reflection of electric waves from the surfaces of transparent media are readily given by these constructions. Thus, if the index $\mu$ of the first medium is less than $\mu_1$ of the second, and the incidence is

not far from normal, we see from Fig. 1 that the amplitudes both for oscillations in and perpendicular to the plane of incidence are measured backwards from $P$, and that in each case the oscillation on reflection loses half a wave-length or is reversed.

As the angle of incidence decreases the angle of refraction decreases, and at nearly normal incidence the tangents and sines become equal to the angles $r \sim i$, $r+i$ and sice $\rho/r = \rho/i$, $R'I = (\rho-\rho_1)/(\rho+\rho_1)$ for both directions of oscillation.
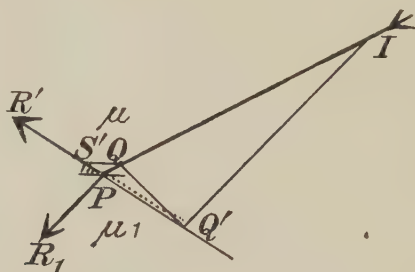


Fig. 2.—Incident Amplitude $PI$, Reflected $PQ'$ and $PS'$.

As the angle of incidence $i$ is increased, $Q$ and $S'$ approach $P$, and the amplitude of the reflected wave when the oscillation is in the plane of incidence decreases. When $Q$ and $S'$ coincides with $P$, the reflected and refracted rays are at right angles, the amplitude is zero, and the reflected ray contains no oscillation in the plane of incidence. We thus get Brewster's law of complete polarisation of the reflected ray for an incident ray of any kind.
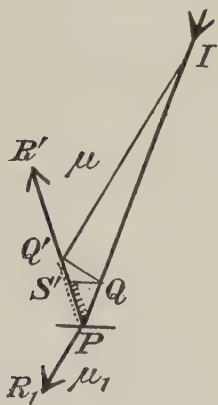


FIG. 3.
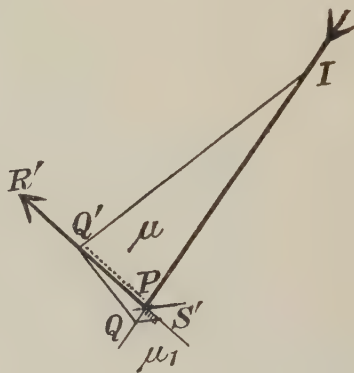
FIG. 4.

INCIDENT AMPLITUDE $PI$, REFLECTED $PQ'$ AND $PS'$.

When the angle of incidence is increased beyond the polarising angle, as in Fig. 2, the construction gives $Q'$ still behind $P$, and the reflected ray losing a half wave-length if the oscillation is perpendicular to the plane of incidence; but $S'$ is now between $P$ and $R'$, and there is, therefore, no loss of half a wave-length for reflection of an oscillation in the plane of incidence.

'As the angle of incidence approaches 90° *PS'* increases rapidly, and at grazing incidence both *PQ'* and *PS'* are equal to *PI*, and the whole of the incident energy is reflected.

### (4.)

When the index $\mu$ of the first exceeds $\mu_1$ of the second medium, the construction (Fig. 3) shows that there is no loss of half a wave-length on reflection in either case, since *Q'* and *S'* lie between *P* and *R'*. As the angle of incidence increases, *S'* approaches *P*, and the amplitude of the oscillation in the plane of incidence diminishes, becoming zero when *S'* coincides with *P*, that is at the Brewsterian angle of incidence, and the reflected ray oscillates in all cases perpendicular to the plane of incidence. For larger angles, *S'* lies behind *P*, showing that there is a loss of half a wave-length on reflection for oscillations in the plane of incidence, although there is no loss for oscillations perpendicular to the plane of incidence (Fig. 4).

When the angle of incidence is further increased, the refracted ray becomes nearly parallel to the reflecting surface (Fig. 5), *PQ'* and *PS'* becoming nearly equal to
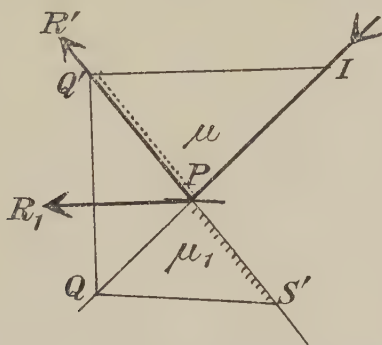


FIG. 5.—INCIDENT AMPLITUDE *PI*, REFLECTED *PQ'* AND *PS'*.

*PI*, and when the refracted ray grazes the surface *PQ'*=*PS'*=*PI*, and the whole of the incident energy goes into the reflected ray.

For angles greater than the critical angle the construction becomes impossible, since there is no refracted ray.

### (5.)

When used in conjunction with any one of the graphical methods of determining the direction of the reflected and refracted rays,* the two constructions solve completely the problem of reflection so far as it is covered by the Fresnel formulæ.

### DISCUSSION.

The PRESIDENT congratulated the author on his elegant construction, which would be welcome both to teachers and pupils.

From Prof. R. Ll. JONES (communicated) : I have used the following method of tracing the variations in the amplitude of the reflected wave given by Fresnel's expressions. Describe a

---

* The method in which two circles or radii proportional to $\mu$ and $\mu_1$ are used, reproduced as Fig. 43 in the Intermediate Practical Physics of Schuster and Lees, is one of the simplest.

circle $AEA'$, centre $O$, and on the diameter $A'A$ take a point $C$, so that $OC=\mu.OA$, $\mu$ being the ratio of the refractive indices of the two media. Through $C$ draw $BCB'$ making, with $OC$, an angle $r$ equal to the angle of refraction. Then $OBB'=i$, the angle of incidence, and $BOC=i-r$. This construction gives Fig. 1 when $\mu>1$, and Fig. 2 when $\mu<1$; the construction is due, I believe, to Tait.

From the two triangles $OBC$, $OB'C$ with the side $OC$ and the angle $r$ in common we get

$$\frac{\sin(i-r)}{\sin(i+r)}=\frac{CB}{CB'}=\frac{CB^2}{CE^2}=\frac{1}{(\mu^2-1)OA^2}\cdot CB^2 \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

where $CE$ is tangent to circle in Fig. 1, and at right angles to $AA'$ in Fig. 2.
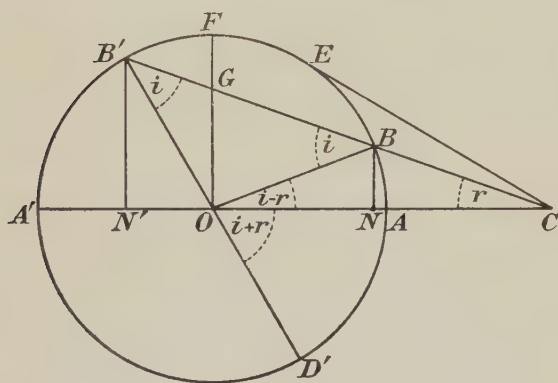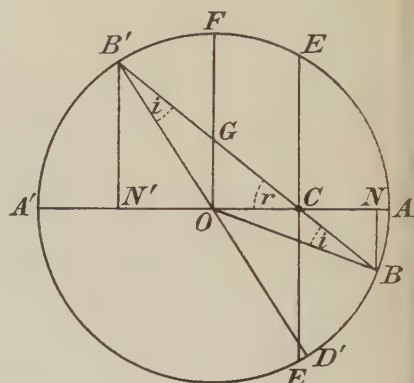


FIG. 1.                                             FIG. 2.

At normal incidence $CB=CA$ and

$$\frac{\sin(i-r)}{\sin(i+r)}=\frac{(\mu-1)^2OA^2}{(\mu^2-1)OA^2}=\frac{\mu-1}{\mu+1}$$

At grazing incidence in the first case and at the critical angle in the second case, $CB=CE$ and the expression $=1$.

For light polarised at right angles to the plane of incidence Fresnel's expression for the amplitude of the reflected vibration is

$$\frac{\tan(i-r)}{\tan(i+r)}$$

From $B$, $B'$ draw $BN$ and $B'N'$ at right angles to $AA'$ and let $OF$ drawn at right angles to $AA'$ meet $CB'$ in $G$. Then we get

$$\frac{\tan(i-r)}{\tan(i+r)}=\frac{BN}{ON}\cdot\frac{ON'}{BN'}=\frac{ON'}{ON}\cdot\frac{BN}{B'N'}=\frac{B'G}{GB}\cdot\frac{CB}{CB'}=\frac{1}{CE^2}\left[\frac{B'G}{BG}\cdot CB^2\right] \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

At normal incidence $B'G=BG$ and $CB=CA$, and the expression becomes $\dfrac{\mu-1}{\mu+1}$.

When $B'$ coincides with $F$ the reflected and refracted rays are at right angles and the value of the expression is zero.

When $B'$ passes through $F$, $B$ and $B'$ are on the same side of $OF$, indicating a change of sign and change of phase of half a period in the reflected ray.

The method given above follows naturally from the construction which Tait* uses to prove the proposition that in any refraction the deviation increases as the angle of incidence increases. The expression for the tangent formula in (2) is rather clumsy as it involves several varying quantities. In the important case of normal or nearly normal incidence (1) and (2) show the value of the amplitude of the reflected vibration in a perfectly clear and unmistakeable form.

Prof. LEES (communicated reply) : It has always seemed to me that the graphical method of finding the refracted ray which depends on two circles with radii equal to the refractive indices was superior to the one Prof. Jones gives in his Fig. 1 and ascribes to Tait. Simple constructions for the Fresnel ratio of sines are easily found. The ratio of tangents gives more trouble and I should endorse Prof. Jones's statement that his expression is " rather clumsy."

* Tait's " Light."

XVIII. *A New Form of High Vacuum Automatic Mercury Pump. By* H. P.
WARAN, *M.A., Ph.D.* (*Government of India Research Scholar of the University of
Madras*).

ABSTRACT.

The pump is based on a modified Sprengel action. It works automatically, the
mercury being removed from the lower to the upper reservoir mixed with a current
of dry air which is sucked through a side tube by a filter pump. The defects of design
of former types of pump are discussed, their inefficiency at low pressures explained,
and suitable simple remedies suggested. The introduction of an intermediate reservoir
in the middle of the fall tube, kept automatically exhausted by the Sprengel action in
the lower fall, allows the upper half to exert a positive exhaustion for every pellet of mer-
cury falling down, even at the lowest obtainable pressure. The absence of compression
in the first fall enables the maximum bore to be used for the fall tube ; and hence speeds
and efficiencies of exhaustion comparable to those of a Gaede pump are obtainable,
though less than a pound of mercury is required to operate the pump.

*Introductory.*

THE rapid production of high vacua is increasingly becoming necessary in modern
work, and the difficulties that confront experimenters in situations where none of the
modern high-class mechanical or mercury pumps are available for the purpose are
only too well known. Any arrangement improvised locally to meet the situation
must satisfy by the nature of the case the principal requirements of simplicity, low
cost, quickness of action, as well as automatic working. A Töpler pump of the
Antropoff or inclined barrel form is convenient enough, though it requires a lot of
mercury as well as constant attention. But a mercury pump that operates on the
old Sprengel principle is evidently the most convenient, since, by the introduction of
the well-known arrangement for the automatic circulation of the mercury, not only
is the pump kept in operation without attention for long periods, but the amount
of mercury required for its working is rendered surprisingly small, if the parts are
properly designed. Further, considering the modern practice of maintaining a
steady suction at one end of an apparatus and balancing it by a steady gas feed at
the other end, such a form of pump has its special advantages for the purpose.

Various forms of automatic mercury pump, of the design of Boltwood, Khal-
baum, and Zehnder, were in use before the advent of the Gæde pump. But these
have not come into general use, since, on account of their defective design, they were
rather slow in action and ineffective at very low pressures. This can easily be seen
by a brief consideration of the working of such a pump using the simple Sprengel
action. When the mercury begins to hammer in the fall tube the situation is as
represented in Fig. 1, and efficient exhaustion then practically ceases. The mercury
stands up to nearly barometric height in the fall tube, and a pellet of mercury falling
down this tube traps the low-pressure gas between $A$ and $B$, compressing it to an
inappreciably thin disc of gas against the head of the mercury column. Finding
downward progress against the atmospheric pressure difficult, this disc gets shattered
into bubbles which stick to the glass walls, and find an easy escape upwards. This
escape back of the gas is facilitated in the automatic types of pump by the oscillatory
motion of the mercury column. The pressure at which this process sets in is deter-
mined solely by the width and height of the effective fall above the barometric height,
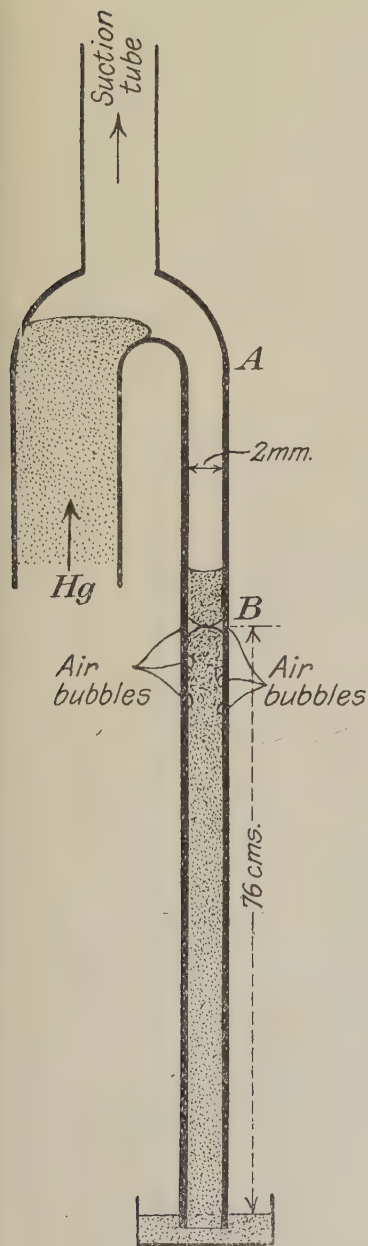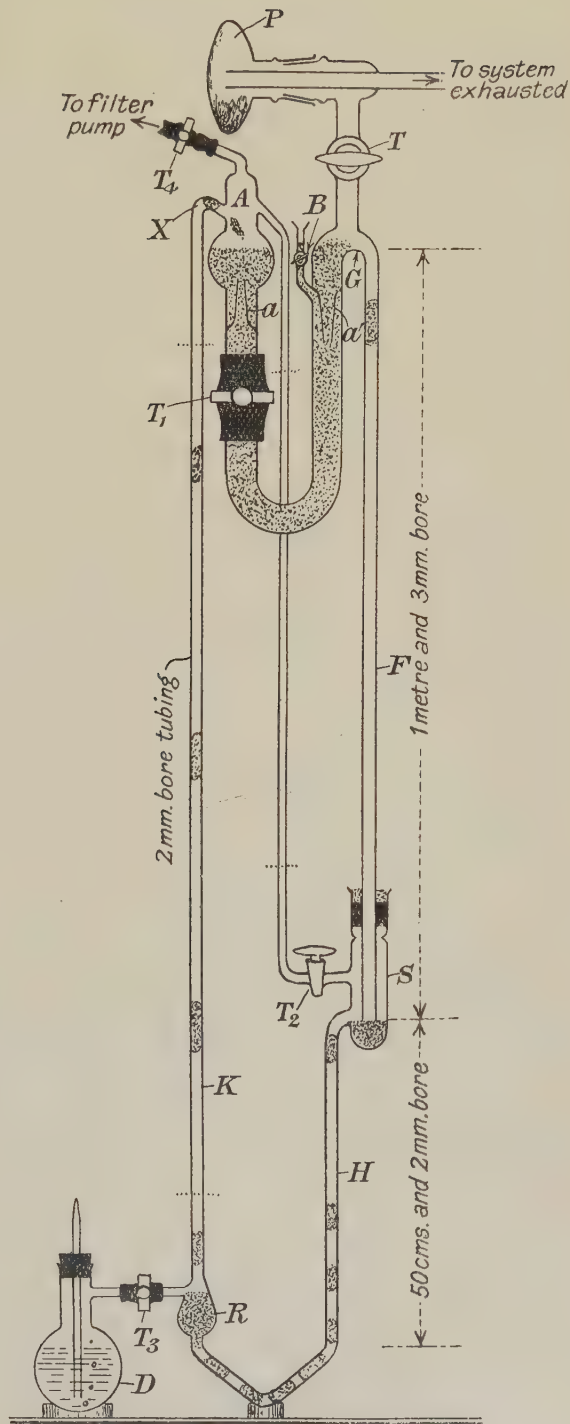
FIG. 1.

FIG. 2.

$P_1$ = Phosphorus pentoxide drying chamber.
$D$ = Drying bottle of concentrated sulphuric acid.
$T_1, T_3, T_4$ = Rubber connections with screw clamps.
$T, T_2, B$ = Vacuum glass stop cocks.

and it is easy to see that by the employment of a greater length and narrower section for the fall tube, a higher vacuum is obtainable (though correspondingly more slowly) before the pump ceases to act on this account.

During some experiments with pumps of this kind it occurred to the writer that this objection could be easily overcome by the following simple device, which carries with it many other advantages. The fall-tube is divided into two sections, the upper one $F$ being longer than the lower one $H$ ; and between them is mounted an intermediate reservoir $S$, as shown in Fig. 2. Tube $F$ is connected to $S$ through a rubber joint, made easily by slipping on a short length of thick-walled rubber tube that makes a tight fit round the outside of the fall tube, as well as inside the tubular reservoir ; the joint being rendered air-tight by a pool of mercury over the rubber forming a mercury seal.

The lower half $H$ of the fall tube is connected to the side of the reservoir $S$, and the projecting end of $F$ inside $S$ so adjusted as to be just below the surface of the pool of mercury in $S$, which is filled to the verge of overflowing into $H$. The fall of mercury now takes place in two stages : the first one in $F$, whereby the pellet of mercury pushes down in front of it the column of rarefied gas into $S$, which is kept automatically exhausted to nearly the same pressure ; and a second one in $H$, whereby this accumulation of gas in $S$ is pumped away whenever it is sufficient in amount for the simple Sprengel action to come into play. In fact the action is very similar to that in a Gæde pump—hence its high efficiency and speed even at very low pressures. The introduction of such a device in the fall tube enables the exhaustion to proceed to limits previously unattainable. (Reference may be made here to an earlier Paper.*)

Another principal trouble with the earlier forms of the pump arises from the large amount of air carried along by the mercury into the vacuum system, partly carried along the walls of the tube, and partly adsorbed. Elaborate devices to guard against the fouling of the vacuum due to this cause are in use in every type of pump working on the Sprengel principle. In the modern automatic types, worked by a filter pump, the vacuum of a few centimetres of mercury at the main reservoir end considerably reduces the amount of such admixed air. I find a pair of traps in a short U-tube in the circuit of the incoming mercury, as indicated at $a$ and $a'$ in Fig. 2, a simple and effective safeguard to break and check the progress of air working along the walls of the tube ; the traces of admixed air being simultaneously eliminated by the filtering operation of the traps. Further, as with a Gæde pump when the rate of exhaustion is sufficiently high, residual minor leakages become quite negligible.

On such lines I have modified my original design of the pump, and have arrived at a compact and simple design illustrated in Fig. 2, the performance of which under ordinary circumstances compares favourably with that of a small size Gæde pump.

### The Working of the Pump.

Keeping $T_1$ open (Fig. 2) the pump is charged with mercury to the levels indicated by pouring it through $B$, which is then closed. On starting the filter pump, with $T$, $T_2$ and $T_4$ open and $T_1$ and $T_3$ closed, it sucks away the system down to a centimetre of mercury in a few minutes through the circuit $PTFST_2AT_4$. After closing $T_2$, if $T_3$ is slightly opened a current of dry air is sucked through $DT_3RKAT_4$, and the back pressure of this makes the level of mercury in $H$ rise about 15 centimetres

* Proc. Indian Association for the Cultivation of Science, Vol. VI., p. 199 (1921).

higher than that in $R$, and this pressure tends to drive the mercury from $A$ into $F$ on opening $T_1$ a little. The mercury from $A$ passes through $a$ and $a'$, and getting rid of the admixed and creeping air in these filters falls down $F$ in pellets which trap columns of air of the volume of $F$, and push them into $S$. If $T_2$ is again opened a little, the gas accumulating in $S$ escapes readily into the filter pump, while the mercury flows down $H$, raising the level in $R$ past the opening from $T_3$. The current of air coming in through $T_3$ pushes this mercury into $K$, and aided by the suction of the filter pump at the other end it goes rapidly up the tube $K$, and on reaching the bend at $X$ the mercury gets shot down into $A$, while the air is sucked away by the filter pump. This action of the pump is automatically maintained ; and in a few minutes, when the pressure has gone down to the order of 0·01 mm. (or earlier if the volume exhausted is small) the tap $T_2$ is closed again. The second fall $H$ now begins to function, rapidly exhausting $S$ and maintaining it at about 0·001 mm. The flow of mercury may now be speeded up to the maximum rate it is possible to use with advantage, allowing for the slow flow of gas through various tubes at such low pressures, and the definite time of fall down $F$. The exhaustion in the present apparatus now proceeds rapidly at the very stage when the usual types cease to act ; for every pellet falling down $F$ produces a positive exhausting effect in $P$ even at the lowest pressures obtainable.

For the most effective and rapid working the relative size of openings of $T_1$ and $T_3$ have to be so adjusted by trial that, with the minimum opening of $T_3$ and the maximum of $T_1$, all the mercury coming down $F$ is transferred back to $A$ from $R$ at the quickest rate, without, however, causing back pressure of mercury in $H$ of more than 30 centimetres. An interesting property of the pump is its capacity of self-adjustment within wide limits in regard to this requirement. For example, if an excess of mercury is coming down $F$ it gets transferred up $K$ rather slowly ; and in the meantime the filter pump, producing a higher vacuum at $A$, reduces the back pressure driving the mercury into $F$, and so the mercury flow becomes automatically reduced.

To stop the pump the taps $T, T_1, T_3,$ and $T_4$ are closed in the order named, before shutting off the filter pump and then its water supply.

Though the pump is easily improvised according to the above design by anyone acquainted with the elements of glass blowing, for its efficient performance a number of minor points have to be attended to, and the few complications introduced into the design have for their object the improvement of the efficiency and quickness of action of the pump. It would take too long to go into the details and considerations that govern the design of each part ; the principal points requiring special attention are, however, briefly outlined below.

The side tube from $S$, containing tap $T_2$, may be dispensed with in the simpler models intended for exhausting small volumes. The object of this side connection is solely to expedite the suction in the preliminary stages. For by opening $T_2$ the filter pump can straight away exhaust the system (up to its limit of about a centimetre of mercury) through $PTFST_2A$, instead of through $PTFSHRA$, in which case it would have to suck against the head of a few centimetres of mercury at $R$. Further, if the system to be exhausted is of any considerable volume, because of the accumulation of gas in $S$ in the preliminary stages at a rate at which the second fall cannot pump it away, the pump cannot be speeded up at once to its full capacity. With the provision of the side connection this accumulation is readily removed by the filter pump, through $T_2$ kept partially open for the purpose ; this tap being completely closed for the final stage of high exhaustion.

If the side connection with tap $T_2$ is provided, it is preferable to have it of narrow bore capillary tubing, so that the fluctuations of pressure in $A$ during the working may not produce any effect at $S$ when $T_2$ is kept partially open in the preliminary stages.

To ensure the rapid automatic circulation of the mercury in the pump the dead capacity on the filter-pump side, *i.e.*, the volume of the air circuit $RKAT_4$ up to the filter-pump, must be made as small as possible.

Though $T$, $B$ and $T_2$ must be good vacuum taps, the others may with advantage be good rubber joints with screw clamps over them, thus providing greater flexibility of adjustment.

The rounded shape of the bend at $G$ is also important, since upon this depends the proper formation of a single large drop of mercury which shall on falling into $F$ form at once an effective plunger.

### Concluding Remarks.

A great advantage secured by the adoption of the modified Sprengel action (above described) is that it enables a high vacuum to be attained at a high speed, because of the large bore and length of fall-tube which it permits. Using a 3 mm. bore fall-tube (in place of the usual one of 1 mm.) and an effective length of 100 cm. (instead of the usually available one of about 50 cm.), and bearing in mind the rate of exhaustion varies directly as the volume of the effective fall, it is readily seen that this form of pump exhausts about twenty-five times as rapidly as the ordinary form of Sprengel pump.

Since the gas is not compressed appreciably in the pumping out process in the first fall, the apparatus is effective against traces of vapours, and thus the limit of exhaustion is as good as, if not better than, that given by a Gæde pump. It requires less than a pound of mercury to run it, while for a Gæde pump about 50 lbs. of mercury must be used. Again, the extra source of power required to work a Gæde pump is dispensed with.

The present design of pump has also the advantage that it can be made or bought in five ready-made units that require only to be mounted rigidly on a stand, and connected up by rubber joints (preferably mercury seated) in positions indicated by the dotted lines in Fig. 2, the use of rubber joints being permissible since they lie on the low vacuum circuit only. (The complete pump, or its component parts ready for mounting, can now be had from Messrs. Baird and Tatlock, Hatton Garden, London.)

A few months ago I had occasion to make and use pumps of this type at the Cavendish Laboratory, Cambridge, for running a 20-ft. hydrogen discharge tube (Prof. R. W. Wood's pattern) of large volume, with a steady gas feed at one end, and its performance was quite satisfactory throughout the few months it was in almost daily use. Connected to other apparatus a degree of exhaustion represented by an alternative gap of about six inches has been obtained without difficulty.

### DISCUSSION.

Mr. R. M. ARCHER : I should like to put three questions to the author. (1) Does he not find that the bottom of the tube $S$ occasionally gets knocked out by the falling mercury ? (2) How long would the pump take to evacuate a space of, say, 1 litre to a pressure of 0·0001 mm. ? If it can do this in a reasonable time it has a great advantage over the Gaede pump, which is apt to get out of order in consequence of leakage of lubricant, etc., and is difficult to put right. Further, the present pump has the advantage of being transparent, and it can be easily kept clean. (3) Can it be used to extract residual gases for analysis ?

Mr. J. GUILD : Would the pump become too complicated if it were provided with several fall-tubes in parallel ?   In an ordinary Sprengel pump it is common to use half a dozen of these, thus compensating for the disadvantage of a narrow bore.   The present apparatus seems to me to demand considerable skill for its construction, whereas a Sprengel pump is generally used by persons who wish to erect a cheap and simple apparatus for themselves.   Is not the apparatus very liable to breakages ?

THE AUTHOR : In reply to Mr. Archer—The tube $S$ does not get broken by the falling mercury—in fact, the bottom of this tube may be of rather thin glass.   I could not say offhand how long the pump would take in the case he gives, but in the case of a space of 500 c.c. it produced a vacuum corresponding to a 4-inch spark-gap in about an hour.   In reply to Mr. Guild— My idea has been to construct a simple pump which anyone can make.   The additional fall-tubes would certainly add to its complexity, and they would also take up more mercury.   I do not think any one possessed of moderate skill in glass-blowing should have much difficulty over the construction.   As regards accidents, I have used four of these pumps and nothing worse has happened than the cutting off of the water supply by some unauthorised person !   The apparatus should not be left idle unless the stop-cocks are turned off, otherwise mercury may get forced into the tube $P$.   It will be noticed that a trap is provided against this contingency—a device which has proved an adequate safeguard.

DEMONSTRATION of an Electrostatic Voltmeter, and of Apparatus for Weighing and Density Determinations, by the Research Staff of the General Electric Co., London.   (Shown by Mr. E. M. EDEN and Dr. F. S. GOUCHER.)

(a) *A Rapid-Weighing Balance* for quantities up to 40 mg. (scale-divisions 0·1 mg.). This instrument is more particularly used for weighing filaments, which are hung on the lever of a torsion balance, thereby tightening a fine vertical wire. To the middle point of the latter is attached one end of a horizontal wire, the other end of which is fixed.   The middle portion of the horizontal wire is optically projected on to a scale.

(b) *Electrostatic Voltmeter.*—This comprises a fixed and a movable disk, the distance apart being adjustable.   The movable disk when attracted tightens a catenary of fine wire, the middle portion of which is optically projected on to a scale.

(c) *Apparatus for the Measurement of Density of Fine Wires.*—The wire to be tested is arranged as a cantilever and the sag of its end is measured in air and in a liquid of known density.

### DISCUSSION ON THE ELECTROSTATIC VOLTMETER.

Prof. C. H. LEES commented on the high damping of the instrument, which contrasts favourably with that of many electrostatic voltmeters.

Mr. C. C. PATERSON remarked that the design in some respects resembles that of Abraham, which also employs sliding electrodes.   The chief novelty of the present instrument lies in the direct measurement of the sag of the catenary.

Mr. K. EDGCUMBE said he should be interested to know how the instrument was calibrated.

Mr. B. S. GOSSLING, in reply to the previous question, stated that the electrometer was standardised by comparison with an electro-dynamometer.   It might be of interest, he added, to give some further details.   A theoretical calculation shows that for very small voltages the scale is somewhat close, but for greater voltages it is more open, and is nearly uniform, closing again as the wire becomes taut.   The calculated scale agrees very well with that obtained by the calibration, and the scales corresponding to different adjustments of the disks agree equally well with one another.   The catenary is so designed that the movement of the small attracted disk is very small compared with its distance from the fixed disk.

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